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1941



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Notice

This volume is the fourteenth of a series containing papers and discussions presented before the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers since its organization in 1928; one volume each year, as follows:

1928, Iron and Steel Technology in 1928 (later listed as Volume 80 of the TRANSACTIONS); 1929 (vol. 84), 1930 (vol. 90), 1931 (vol. 95), 1932 (vol. 100), 1933, 1934, 1935, 1936, 1937, 1938, 1939, 1940 and 1941, TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Iron and Steel Division.

This volume contains papers and discussions presented at the meetings at New York, Feb. 12-15, 1940; Pittsburgh, Apr. 24-26, 1940; Cleveland, Oct. 21-23, 1940; New York, Feb. 17-20, 1941.

Papers on iron and steel subjects published by the Institute prior to 1928 are to be found in many volumes of the TRANSACTIONS of the Institute; in Vols. 37 to 45, inclusive; 47, 50 and 51, 53, 56, 58, 62, 67 to 71, inclusive; 73 and 75. Vol. 67 was devoted exclusively to iron and steel.

Iron and steel papers published in the TRANSACTIONS before the year 1936 may be found by consulting the general indexes to Vols. 1 to 35 (1871-1904), Vols. 36 to 55 (1905-1916), Vols. 56 to 72 (1917-1925), and Vols. 73 to 117 (1926-1935).

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FOREWORD

THIS volume of the TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers is, as usual, about equally divided between papers dealing with iron and steelmaking and with physical metallurgy.

Dr. A. V. DeForest's Howe lecture on Some Complexities of Impact Strength leads the list of papers on physical metallurgy, and in addition there are fourteen papers covering a wide range of interest in this field.

In the steelmaking papers it is most interesting to note that five of the thirteen are on the Bessemer process, an indication of the greatly developed interest in this process recently. Of the other steelmaking papers, another symposium on steel-making reactions centered largely around the question of slag-metal reactions, a subject that is of ever recurrent interest. The other papers on iron and steel are devoted to ore concentration, pig-iron practice, and rolling-mill operation.

The Open Hearth Committee held its Third Joint Conference with the Blast Furnace and Raw Materials Committee in Chicago with a record-breaking attendance.

Taken altogether, the papers in this volume together with the PROCEEDINGS of the Open Hearth Conference constitute a comprehensive and worth-while addition to our literature on iron and steel metallurgy.

C. H. HERTY, JR., *Chairman,*
Iron and Steel Division.

BETHLEHEM, PA.,
August 3, 1941.

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The Howe Memorial Lecture

THE Howe Memorial Lecture was authorized in April 1923, in memory of Henry Marion Howe, as an annual address to be delivered by invitation under the auspices of the Institute by an individual of recognized and outstanding attainment in the science and practice of iron and steel metallurgy or metallography, chosen by the Board of Directors upon recommendation of the Iron and Steel Division.

So far, only American metallurgists have been invited to deliver the Howe lecture. It is believed that this lecture would gain in importance and significance were it possible to include metallurgists from other countries, but the Institute has not yet been able to do this on account of lack of special funds to support this lectureship.

The titles of the lectures and the lecturers are as follows:

- 1924 What is Steel? By Albert Sauveur.
- 1925 Austenite and Austenitic Steels. By John A. Mathews.
- 1926 Twenty-five Years of Metallography. By William Campbell.
- 1927 Alloy Steels. By Bradley Stoughton.
- 1928 Significance of the Simple Steel Analysis. By Henry D. Hibbard.
- 1929 Studies of Hadfield's Manganese Steel with the High-power Microscope. By John Howe Hall.
- 1930 The Future of the American Iron and Steel Industry. By Zay Jeffries.
- 1931 On the Art of Metallography. By Francis F. Lucas.
- 1932 On the Rates of Reactions in Solid Steel. By Edgar C. Bain.
- 1933 Steelmaking Processes. By George B. Waterhouse.
- 1934 The Corrosion Problem with Respect to Iron and Steel. By Frank N. Speller.
- 1935 Problems of Steel Melting. By Earl C. Smith.
- 1936 Correlation between Metallography and Mechanical Testing. By H. F. Moore.
- 1937 Progress in Improvement of Cast Iron and Use of Alloys in Iron. By Paul D. Merica.
- 1938 On the Allotropy of Stainless Steels. By Frederick Mark Becket.
- 1939 Some Things We Don't Know about the Creep of Metals. By H. W. Gillett.
- 1940 Slag Control. By C. H. Herty, Jr.
- 1941 Some Complexities of Impact Strength. By Alfred V. de Forest.

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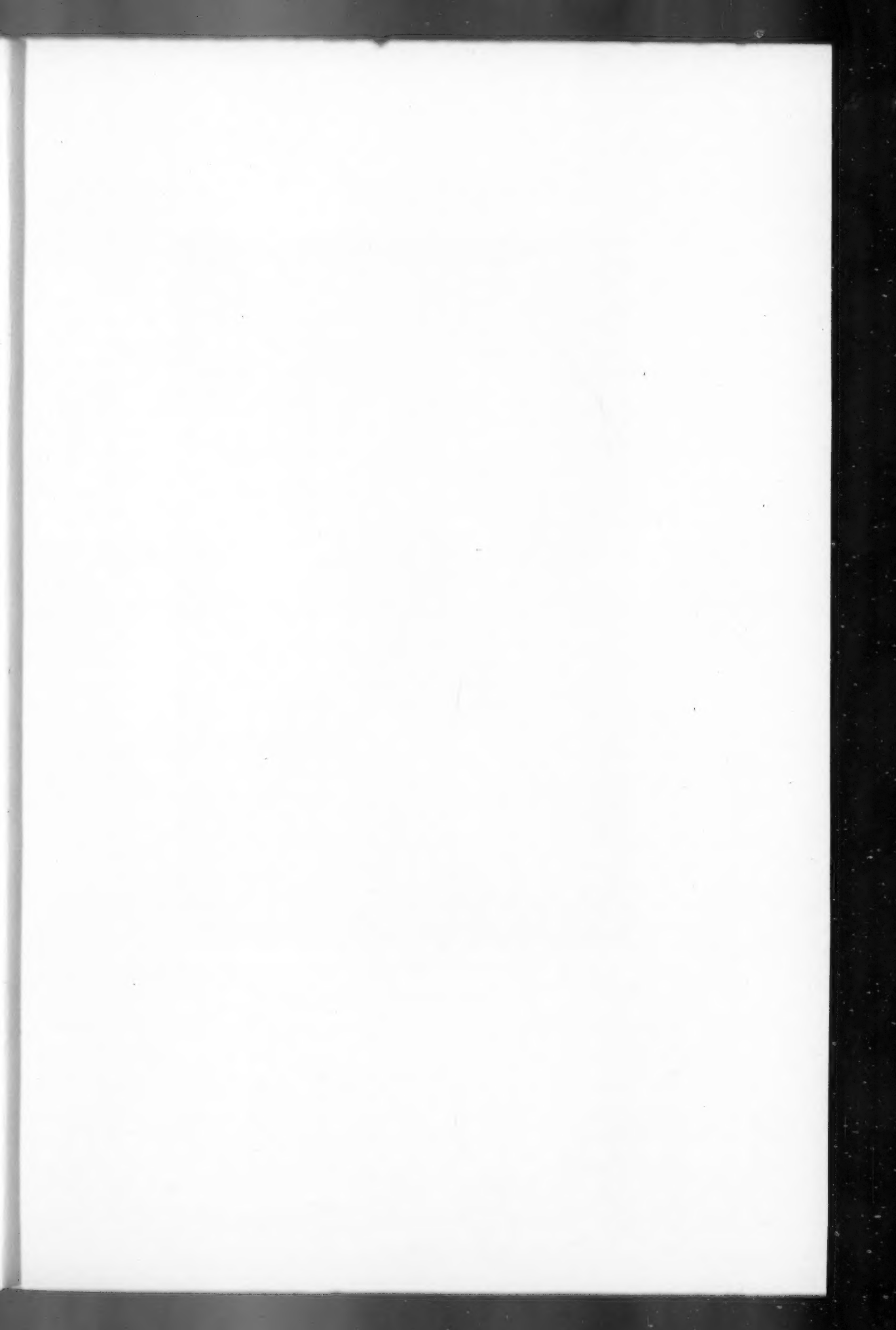
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ALFRED V. DE FOREST

Henry Marion Howe Memorial Lecturer, 1941

Some Complexities of Impact Strength

BY ALFRED V. DE FOREST,* MEMBER A.I.M.E.

(Henry Marion Howe Memorial Lecture†)

WE are now assembled in this hall for the eighteenth lecture in honor of the memory of our greatest American metallurgist, Henry Marion Howe. Many of his most intimate contemporaries, led, as was fitting, by Professor Sauveur, have described his vital accomplishments in three fields: as a leader in technical industrial development; in theoretical research; and finally as a teacher and source of inspiration for nearly two generations of students.

In 1914 Professor Howe had retired from active teaching, but maintained his laboratory at Columbia University under the care of Arthur G. Levy, with whom he published many of the papers that later were incorporated into his last book, "The Metallography of Steel and Cast Iron." My position at the time was that of personal assistant to Professor Campbell—no pay, no duties, but the great privilege of preparing specimens, taking pictures and attending to some of the current consulting work.

Whenever possible, I visited Howe's laboratory to chat with Levy and gather ideas about the wonderful field of metallography—in which I was a rank amateur, rescued by the quiet enthusiasm of Donald Smith of Princeton from an instructorship in civil engineering. Levy let me act as a fly on the wall during the Professor's occasional visits. Busy as he was, Professor Howe took the time and trouble to encourage my interest, as he had done for hun-

dreds of others. He told me how he went about gathering his own information speculating as to causes, considering experiments, and verifying his conclusions. I ventured to mention some tests I had run on the irregular stretching of wires of different metals. He read the small volume I had prepared of ill-assorted facts and fancies and remarked: "Nobody cares for your theories or the history of your tests. Describe what you found as briefly as possible and perhaps I can help you to publish."

Curiously enough, among my discards were some autographically recorded load-versus-electrical-resistance measurements. Taken with inadequate knowledge and equipment, these curves did not reproduce consistently, but if the relationship between strain and resistance had then been explored, the latest type of strain gauge might have been in useful service for the past 25 years.

Professor Howe was a gifted teacher, perhaps because he was primarily an ardent and assiduous student. His own eagerness to learn and his willingness to revise and extend his opinions constantly encouraged those of his environment to be diligent and painstaking in the pursuit of knowledge. In honoring his memory, I also wish to bring to mind the kindly, humorous and quiet Levy, and join his name again, as it was for too brief a space in the past, with that of many-sided Henry Marion Howe.

FACTORS OF IMPACT STRENGTH

The subject chosen for the Howe Memorial Lecture by Dr. Gillett last year

* Professor, Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

† Presented at the New York Meeting, February 1941. Eighteenth Annual Lecture. Manuscript received at the office of the Institute Feb. 20, 1941. Issued as T.P. 1341 in METALS TECHNOLOGY, August 1941.

was the effect on metals of loads long sustained, particularly by steel at elevated temperature. Another aspect of the strength of metals lies in their reaction to suddenly applied load, variously called shock and impact. Occasional structural failures under such conditions have long engaged the attention of engineers and metallurgists, who have postulated the special term, impact strength, the lack of which leads to disaster.

Many unknown variables are involved in fatigue strength, but at least the problem at issue has been defined, methods of test devised, and such variables as surface conditions, speed, temperature, corrosive environment, size and notch effect, as modifying a basic endurance limit, are clearly recognized. Impact strength of a structure is a complicated summation of many factors, which seldom may be sufficiently separated to permit of independent study. The difficulties of such an analysis are here presented to your attention in the hope that recent developments in instrumentation will be usefully applied in this field.

Metallurgists of Réaumur's time, about 1720, judged materials almost entirely by the nick bend test and from the results of this test and the type of fracture revealed could distinguish the steel and wrought iron made in any part of Europe. Before the introduction of macroetching and microetching, the appearance of fractured surfaces formed the basis for estimating many important properties of steel, and care and experience in such examination is even now extremely useful. Perhaps the old skill in judgment survives in the present-day fracture test of samples from the open hearth, which seem so mysterious to the disciple of quantitative measurements.

With his universal interest in metallurgy and the strength of materials, Professor Howe added to the clarity of perception of this impact field. Indeed, in his discussion of a paper before this society by John

Howe Hall¹ on shock tests of cast steel in 1913 he sums up the general opinion of our own time. Briefly, Howe's discussion² contains the following important points: Impact resistance, and its converse, fragility, is the name of a particular manifestation of strength; ductility and its converse, brittleness, are used in the conventional meaning as applying to slow rates of loading. Measurements of impact resistance are confined to conventional impact machines measuring the work done in bending specimens with standard notches. Fragility as distinguished from brittleness has disappeared from our vocabulary, but its converse has remained.

USEFULNESS OF TESTS

Howe regarded the, even then, long-standing debate as to the value of the impact test as raising two questions: (1) Does the impact test teach anything that cannot be learned more rapidly from any other test? (2) Is its special teaching of value? His general answer to these questions may be summed up in the statement that, while in many cases impact tests and the work done in breaking a tensile bar reveal the same characteristics of material, there are other cases in which the tests diverge and in the case of divergence there is a reason to be found in the microstructure. To the question as to the value of the special teaching—that is, whether or not the impact test reveals properties of interest to the engineer—Howe quotes a relationship between impact and fatigue strength of marine shafting, steam-hammer rods and armor plate. Elsewhere in the discussion Bradley Stoughton refers to the impact test as discriminating between good and bad heat-treatment of gears. Hall's paper and several of the discussers agree that the notched-bar impact test discriminates between coarse-grained and fine-grained structures in cast

¹ References are at the end of the paper.

and forged material and that the distinction between the different grain structures is not found in the conventional tensile figures. All of these findings, except the relation between impact and fatigue, are well supported by present-day opinion.

Howe further examines the effect of the speed of impact on the results of the test and quotes a number of observations in which a speed effect is apparent and a number of others in which it is not. His opinion on this subject is: "Thus the present evidence as to the influence of the rate of straining is contradictory, suggesting that accelerating the straining has more than one immediate effect and that the sign of these effects is not constant, so that the resultant effect may vary in sign or may be nil." This opinion is still valid.

The range of speed in the observations quoted was relatively small, the highest speed mentioned being only that of a freely falling weight dropping 4 meters, or 29 ft., per second. Howe suggested that the value of impact testing would be greater if the elastic limit under impact could be measured as well as the total work done. Fortunately, convenient means for making this measurement have recently been devised.

Notched-bar Test

Since Howe's time, a great clarification of the notched-bar impact test has been accomplished by considering the special stress distribution due to the presence of the notch. Hoyt,³ in a series of papers, has summarized the situation by showing that the stress conditions at the notch, whether in impact or under slow loading, result in a distribution of stress very different from that in the simple tensile test. The fibers at the extreme bottom of the notch are under longitudinal tension and at the same time are constrained by the transverse stiffness of the metal in such a way that a large transverse tension also

acts on these fibers. The geometry of the notched bar becomes a very powerful influence on modifying the stress conditions under which the most strained fibers are constrained to act.

Hoyt points out that a large amount of evidence supports the view that materials that behave substantially alike under simple stress may behave quite differently under combined stress. He quotes the results of Moser that the narrower the proportions of the notched bar, the more closely the material behaves as in a tension test, but that as the width of the bar is increased, some materials become brittle at a particular width of bar whereas others retain a high degree of ductility. Thus, if the width of the bar is increased by the ratio of three to one in some steels, the work of rupture may be multiplied by a factor of three and in other cases the work of rupture may be reduced to half that of the original bar. It thus becomes apparent that a hitherto little appreciated property of materials is brought into play in the notched bar. This property evidently is the ability of material to exhibit plastic deformation under different degrees of constraint. While the constraint due to multiaxial stress is an inevitably complicating condition in notched-bar testing, many other cases may be found in which the effect of stress or constraint at right angles to the major stress becomes of paramount importance. Curiously enough, in the same discussion of Hall's paper, Webster quotes some cold-bending tests on unnotched steel sections, as follows:

I would like to call attention to the fact that the results of the ordinary tension and bend tests do not always give us the information we want even if we figure out the amount of work done. You want a bending test of sufficient width and full thickness. In the case of eye-bars, for instance, I have had experience with a 10- by 1-in. eyebar which gave perfectly good results in a full-size test of the finished bar. The 10- by 1.5-in. and 10- by 1.75-in.

eyebars from the same heats of steel were absolutely worthless in full-size tests. The narrow bending tests from all these bars gave good results. But after going into the matter fully, we found that if pieces about 3 in. wide and full thickness were used for the cold bending tests, the heavier material would not stand this test, but failed. That is, in order to check the quality of the rolled bar you should have a wide piece of full thickness for cold bending, as the narrow pieces give misleading results.

As I read this discussion it becomes evident that Webster was observing a phenomenon that is frequently met with in the bending of heavy plate; that is, that the thicker and wider the plate, the smaller the angle through which it may be bent, owing, of course, to the added transverse stress on the extreme fiber in tension.

Ductility, and hence energy absorption, may take place only by a shear flow or plastic deformation of the metal involved. This shear cannot take place at all when there are equal tensile stresses along all three major axes. In the ideal tensile test, metal is free to shear along both planes at right angles to the major stress. If there is a state of biaxial stress of equal magnitude in two directions, all the deformation must take place in changing the thickness of the material. This condition of biaxial stress is met in a hollow sphere under internal pressure.

At the present time it is clearly recognized that multiaxial conditions of stress constitute the essential difference between notch-bar testing and tensile testing and that the type of loading of the notch-bar specimen, whether by slowly applied load or by impact, is merely a complicating factor in the case. First it is necessary to understand the ductility of materials under multiaxial stress conditions and then separately and independently to ascertain whether or not there is any effect on this property due to elevated rates of loading. The complexities involved are well summed up in references 4 to 9 (p. 28).

A very simple statement of the problem might be made as follows: To properly define the strength of a ductile material, in addition to the normal tensile or uniaxial strain condition, the degree of constraint necessary to just cause brittle failure should also be defined. Any system of stress distribution that causes brittle failure involves cohesive strength, but no generally accepted method of test for this property has been evolved. Conditions that lead toward more and more constraint are primarily attained by varying the proportions of notches, as in the ordinary Charpy test specimen with variable width, or by a notched specimen of C shape for slow rates of loading due to Professor Haigh¹⁰ (Fig. 1). In this specimen the thickness may be varied in successive tests until an increased degree of constraint causes a brittle fracture. Another test specimen due to Haigh¹¹ is of circular section, so designed as to approach three-dimensional tension, and results in a brittle failure in the most ductile steels. The very complicated conditions to be met in testing under multiaxial stress were ably described by Dr. Gensamer in a series of lectures before the American Society for Metals in October 1940. Cohesive strength and triaxial conditions in general have been investigated by Kuntz⁵ as well as by Davidenkov,⁶ and are fully reviewed by Hoyt,³ by McAdam⁷ and by Sachs.⁸

Long before the era of quantitative testing, the effect on steel of lowered temperature was observed. One of the great contributions of notch-bar impact testing has been the observation that, while ductility under tensile conditions is not seriously affected, ductility under combined stress may altogether disappear at temperatures approaching zero degrees Fahrenheit.

Tests without Notch Effect

While the impact test has primarily been applied to bent specimens, other studies have been made in tensile impact

without notch effect. Mann¹² and Nadai¹³ have both constructed rotating flywheel machines in which high rates of loading are possible. Mann's machine, like previous

indicate that steel under tensile load in an unnotched condition at room temperature approaches a brittle failure at increased rates of loading. Many observations of

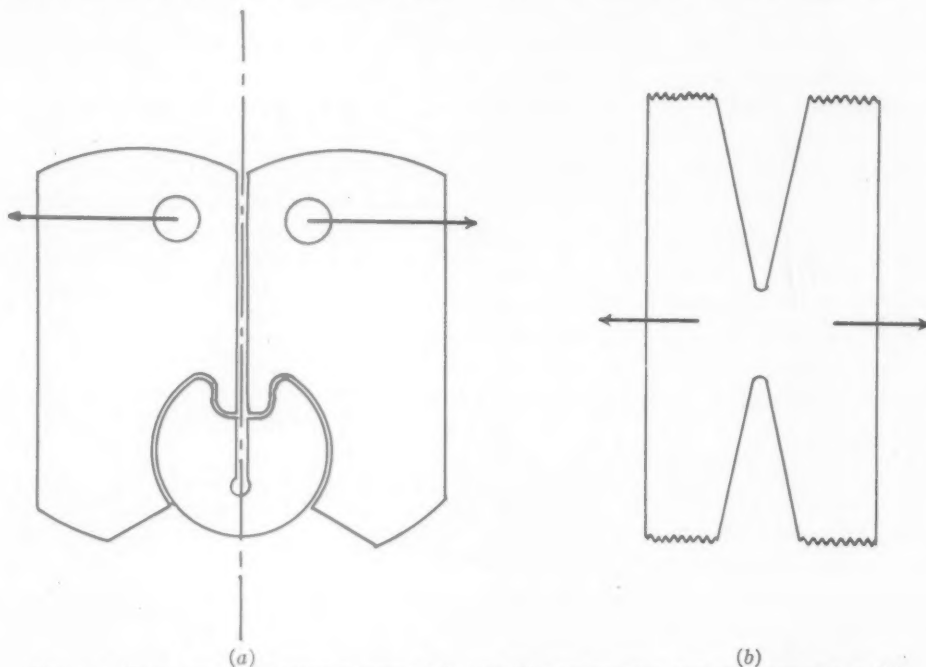


FIG. 1.—DISK-TYPE TENSILE TESTER (a) AND HAIGH TRIPLE-STRESS TEST PIECE (b).

impact machines, records only the work done in breaking the bar, whereas Nadai weighs the instantaneous load on the test specimen together with its rate of elongation. Mann reports that in some steels the work done in breaking the specimen remains constant up to a definite speed, above which the work done decreases as the speed is increased, although the percentage elongation remains approximately constant. This effect therefore is of a different nature from the speed effect in notch-bar testing, where decreased energy absorption is a function of lowered ductility. Nadai's tests on a variety of metals at various temperatures shows that the breaking strength increases progressively as the rate of loading is increased, but finds no evidence of a so-called critical speed. He has, however, not as yet reported on speeds and materials in the same range as those of Mann. No evidence is found to

damage caused by projectiles are noteworthy as showing great ductility even under conditions where severe constraint seemed inevitable. Unquestionably the speed effect is primarily important in the case of severe constraint, and the degree of constraint is more important than the speed. The possible importance, however, of Mann's critical speed must not be overlooked.

Variables

The general picture of impact and notch-bar testing is that for a given steel ductile in simple tension, a degree of constraint may be caused by size and shape of specimen that will produce brittle failure. Lowering the temperature below that of the usual "room" will cause brittleness to appear with less constraint; but whether these variables are truly interchangeable over a variety of steel is highly ques-

tionable. Finally, an increased rate of loading may act in the same manner as reducing the temperature or increasing the constraint. However, many cases are reported in which two steels respond differently to the speed effect. As Howe says, the evidence is conflicting on this point.

It is evident that the three variables of constraint, temperature and speed, must be handled separately before their full relationship is understood. Two distinct methods of investigation may be considered. Assuming that a test piece such as Haigh's "triple stress" specimen, or Gensamer's fatigue-crack notch, will give the cohesive strength or some figure having a close relation thereto, the effect of temperature and rate of loading could be measured to compare with the shear strength as measured under similar conditions. The hope of such a procedure led to the development of high-speed strain-measuring equipment at the Massachusetts Institute of Technology.

Another method, which has long been evident and only incompletely explored, entails more extensive experimentation but less experimental difficulty. Notched specimens, perhaps of Haigh's *C* shape, and with increasing thicknesses and hence with increasing constraint, may be used to determine the dimensions required at different temperatures to just reach the transition between ductile and brittle failure. Then the effect of rate of loading and temperature on this transition condition may be studied separately. It is here assumed that at the critical condition the cohesive and shear strength are equal.

Either program is of appalling magnitude when it is realized that in dealing with rolled steel the direction of the grain in relation to the applied stress exerts a profound effect. However, this effect must be studied, for the very conditions we wish to understand imply at least biaxial loading, and failure will be produced along the

weakest dimension. I have seen a case of this kind in seamless alloy steel tubing, which was sometimes brittle transversely and sometimes longitudinally, with good ductility in the other dimension; in other words, with extreme directional brittleness.

EFFECT OF DIMENSIONS OF SPECIMEN

Turning now from test specimens to full-size structures, we find that the degree of constraint becomes rapidly greater as the dimensions, and particularly the thickness of the parts, is increased. Haigh gives the following table:¹⁰

Size of Square Bar, Mm.	Depth of V Notch, Mm.	Angle Bent to Fracture, Deg.
100	20	8
50	10	14
20	4	38
10	2	75

He remarks: "The practical observation, confirmed by this investigation and equally by further tests on other samples, is of far-reaching importance. Large notched bars are necessarily brittle, even at ordinary temperatures, no matter how toughly ductile the metal may appear when tested in small size pieces." This lack of ductility is especially true in the case of large welded structures and is certainly a factor in a number of recent failures of welded bridges in Germany, Belgium and Holland.

Conditions for such failures are extremely complicated, as the separate roles of stress distribution and constraint are modified by imperfections and notch conditions in the welds and by residual internal stresses of unpredictable magnitudes and directions. The most striking similarity in all the failures was their occurrence in cold weather and the fact that such structures cannot be stress-relieved, as ordinarily is done in smaller welded parts such as pressure vessels.

MEASUREMENT OF LOAD

Considering the impact as apart from the static strength of structures, the most important difference lies not in the speed effect on the strength of the metal, but

Strain Gauges

The measurement of loads applied under impact conditions has received a good deal of attention, but until recently strain gauges that would operate rapidly enough

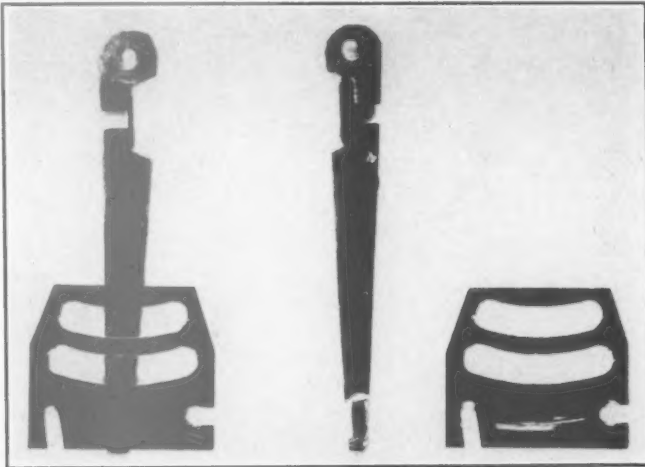


FIG. 2.—STRAIN GAUGE.

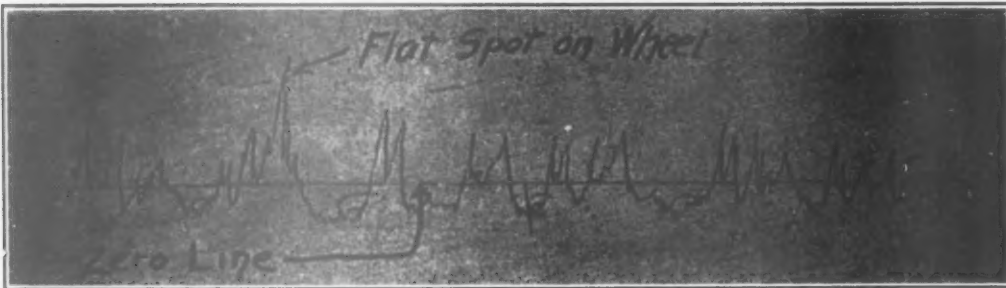


FIG. 3.—SCRATCH RECORD MADE BY GAUGE SHOWN IN FIG. 2.

in the distribution and severity of load applied. The effect of a wheel striking a rail, for instance, involves not only the speed and weight of the axle and wheel, but the details of its many natural periods of vibration. The track stress is also dependent on the very complicated support and springiness of the fish plates, ties, ballast and the earth beneath. A frozen roadbed may double the track stress, and in similar but reverse fashion, ballast on a railroad bridge may reduce the bridge stresses by a similar factor. It is appropriate, therefore, to consider methods of measuring these complicated conditions.

to record the phenomena have not been available. One form of gauge widely used on stresses in rails under the impact of flat wheels, and which has been applied to coupler bars and bridges, consists in a scratch-recording system where the elastic elongation of the metal over a 2 to 4-in. gauge length is recorded directly by pulling an arm, charged with emery, over a polished target (Fig. 2). The scratch record, showing the strains in a steel rail, is illustrated in Fig. 3. Owing to its construction, no time axis is available for this gauge, and only the maximums and minimums are given, but in many cases the simplicity of

the method renders this a convenient form of measurement.

A more recent strain gauge makes use of the change in electrical resistance in a

graphite bonded in Bakelite is cemented to the metal surface and the change in resistance is found to be closely proportional to the strain imposed on the metal. This

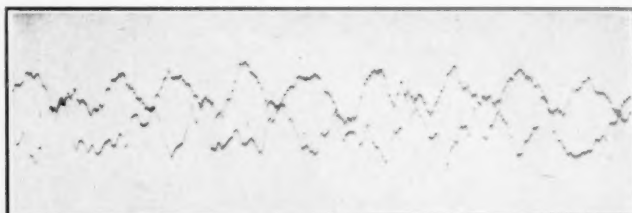


FIG. 4.—RECORD MADE BY GAUGE USED IN STUDY OF VIBRATION OF AIRPLANE PROPELLERS.

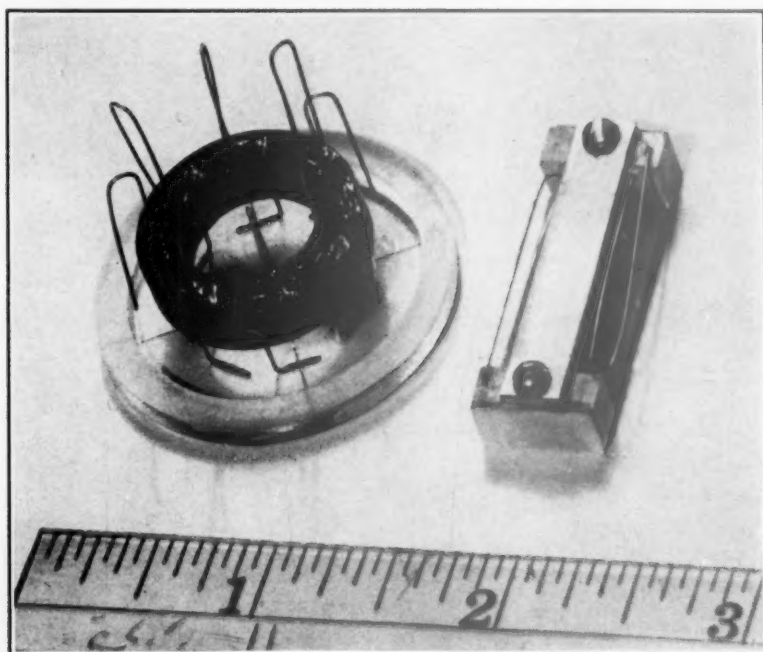


FIG. 5.—STRAIN ROSETTE AND LONGITUDINAL GAUGE.

strained wire. The fact that the electrical resistance of a wire depends on its longitudinal strain was first described by Lord Kelvin.¹⁴ Later Bridgman¹⁵ utilized this change in resistance of wire as a means of measuring hydrostatic pressures and investigated the property of strain sensitivity.

Resistance wire gauges are also used by Carlson.¹⁶ Another form of resistance gauge makes use of the change under strain of a resistor containing carbon particles as its essential conducting medium. In one form of this gauge, finely divided

gauge has been described in a study of the vibration characteristics of airplane propellers¹⁷ (Fig. 4). While the carbon gauge of this general type is useful for dynamic conditions, its behavior under static loads shows some hysteresis. In other words, the change in electrical resistance is not instantaneously proportional to the applied deformation. Finally, Clark¹⁸ and his associates, and Ruge¹⁹ used wires cemented down to the metal surface. In this case, although the strain sensitivity is less, there is no observable hysteresis and the

wire appears to change its resistance instantaneously with the applied deformation. Tests have been conducted up to thirty thousand cycles per second without showing any speed effect.

selected it has been found that the calibration is sufficiently accurate so that the sensitivity factor may be depended upon to plus or minus 1 per cent. For static use no amplifier is needed and a simple resist-

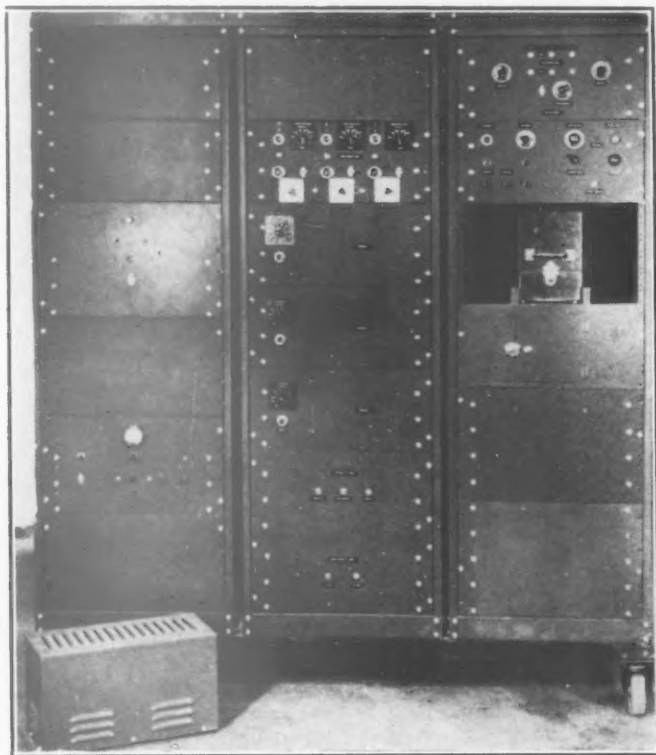


FIG. 6.—THREE-ELEMENT CATHODE-RAY OSCILLOGRAPH.

The wire gauge represents the most versatile yet produced. The active element in the form of wire one thousandth of an inch in diameter, embedded in an insulating cement or a baked-on varnish, is capable of withstanding the highest acceleration, having only an infinitesimal mass and being firmly attached throughout its whole length. The gauge may be of any shape and conform to surfaces of single or double curvature. Gauges may be placed in any direction on the metal and the different component of strain may be measured independently. A strain rosette and a longitudinal gauge are illustrated in Fig. 5.

Many hundreds of gauges have been tested and when the wire has been properly

ance bridge may be used for measuring stresses down to 30 lb. per square inch in steel. This represents the measurement of strain to one part in a million, an order of sensitivity hitherto attainable only by interferometer methods.

For dynamic use the output of the bridge can be amplified and recorded on any suitable oscillograph. In order to study high rates of deformation a three-element cathode-ray oscillograph and associated amplifiers has been developed at the Massachusetts Institute of Technology. This device photographs the oscillograph record on 35-mm. film with a drum camera and produces records that are quite satisfactory when enlarged to a time basis of

4 in. per thousandth of a second. The rate of motion of the oscillograph light spot over this enlarged record may correspond to 13,000 ft. per sec., or 153 miles per

tension wave from the free end, and return to the point of impact.

A more complicated case is illustrated in Fig. 9. A bar 8 ft. long has a diameter of

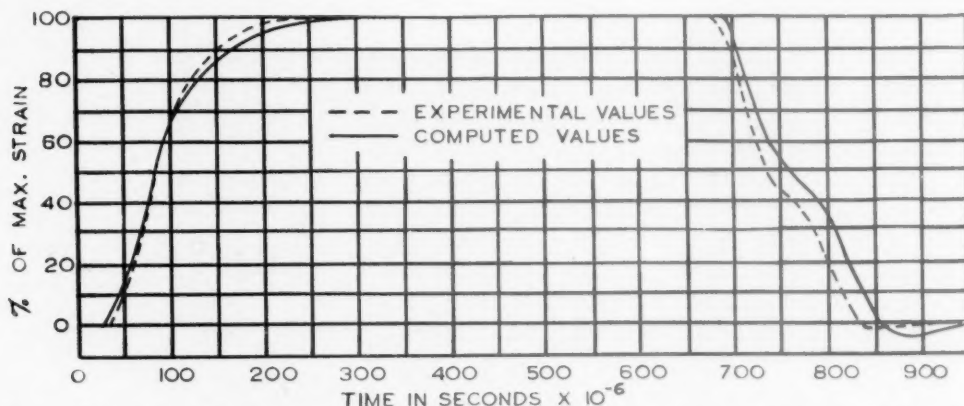


FIG. 7.—SHAPE OF COMPRESSION WAVE AS COMPUTED BY SEARS AND AS MEASURED BY CARBON-RESISTOR ELEMENT.

minute. This oscillograph is shown in Fig. 6.

Results of Tests

The simplest possible problem concerning impact waves traveling through solid material is that of two long bars suspended as longitudinal bifilar pendulums and one bar allowed to swing into collision with the other. The impulse wave generated at the contact is propagated approximately at 17,000 ft. per sec. through both bars. This case was investigated mathematically by both St. Venant and Hertz under different assumptions of the loading conditions at the point of impact. However, Sears^{20,21} gives the most complete solution of the problem. Fig. 7 shows the shape of the compression wave as computed by Sears and as measured by a carbon-resistor element. Fig. 8 shows the shape of this pressure pulse close to the point of impact, at the center of the bar, and close to the free end, as well as a record showing the length of time during which the bars are in contact. This length of time is exactly that required for the pressure pulse to travel the length of the bar, reflect as a

$1\frac{1}{16}$ in. for half its length and $\frac{9}{16}$ in. for the other 4 ft. Three gauges have been applied, one 2 ft. from each end and one very close to the shoulder in the center. The impact is applied by a $\frac{1}{2}$ -ft. bar at the small-diameter end, traveling 5 ft. per sec. at impact. The compression wave passing gauge No. 3 has the wave form shown at the point *A*, being a simple pulse of pressure, the time duration of which is determined by the length of the striker bar. On reaching the shoulder at the center of the bar at point *M*, a portion of the pressure wave is reflected as a compression due to the fixed end condition at *M*, and produces the minor pressure pulse *B*. This minor pulse is reflected as tension from the open end at the point of impact and returns to the gauge 3 as a tension of exactly the same wave form and amplitude, resulting in the tension pulse *d*. Meanwhile, the portion of the pressure wave that was not reflected at *M* has been reflected as a tension at the large-diameter end of the bar. This tension wave is recorded by the tension pulse *F*, which is composed of both the wave that has traveled to the large end and the reflection of pulse *d* from the

shoulder, arriving simultaneously at gauge 3 and traveling toward the small-diameter end. It is reflected from the open end, as a compression wave exactly duplicating

form cross section. As the gauge is at equal distances at both ends, the distance apart of the pulses is uniform. The record shows that the tension and compression are equal.

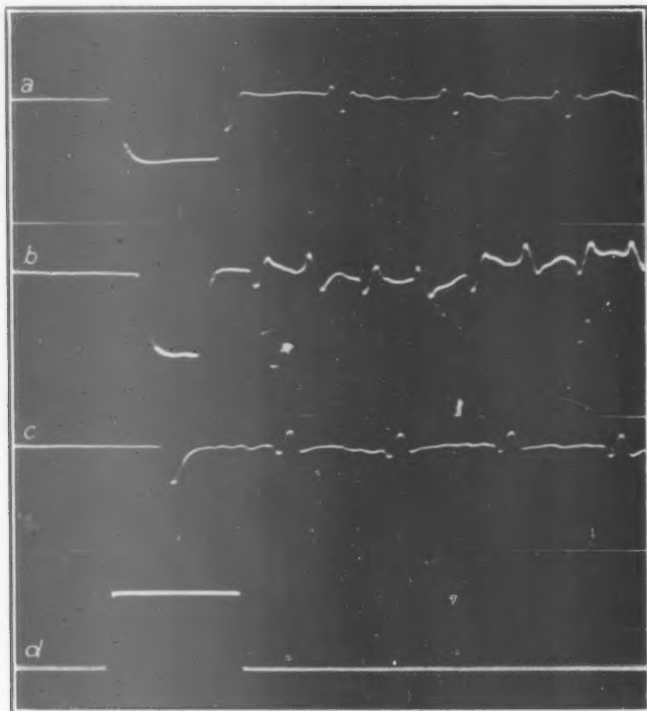


FIG. 8.—SHAPE OF PRESSURE PULSE OF FIG. 7 AND RECORD OF LENGTH OF TIME BARS ARE IN CONTACT.

- a*, close to point of impact.
- b*, at center of bar.
- c*, close to free end.
- d*, length of time.

the previous cycle, as shown in the figure, which records five such pulses.

The condition at gauge 2, close to the shoulder and at the mid-point of the long bar, is simpler. The pressure pulse generated by the impact passes this point as a short compression pulse, similar to *a* of record 3. This pressure pulse is reflected from the large end of the bar as a tension and returns as a simple tension pulse *G*. Gauge 2 is so close to the shoulder that no reflection is measured at this point. Alternate pulses of tension and compression, traveling the full length of the bar, are recorded by this gauge. Conditions here are exactly the same as in any bar of uni-

Gauge 1, at the mid-point of the large-diametered portion of the bar, records the portion of the compression pulse *C*, which has been reflected at the shoulder *M*, passing as a compression wave toward the free end, where it is reflected as tension and returns as a tension pulse at *E*. This wave *e* is not followed by any reflection from the shoulder. This is puzzling until it is realized that at the instant of reaching *M* this tension is met by a similar tension wave *d*, arriving from the small end, as shown in Fig. 10. The shoulder *M*, in a state of tension over a portion of its area, does not reflect the normal compression wave. The whole wave energy passes to the small

end of the bar, resulting in pulse *f*, record 3, the open end reflection of which starts the new cycle. After this pulse has passed, the bar is completely unloaded until the

B and *C*, etc. The steepness of the wave front is evident. An interesting property of long bars is illustrated here. The pressure conditions at the end of the bar are

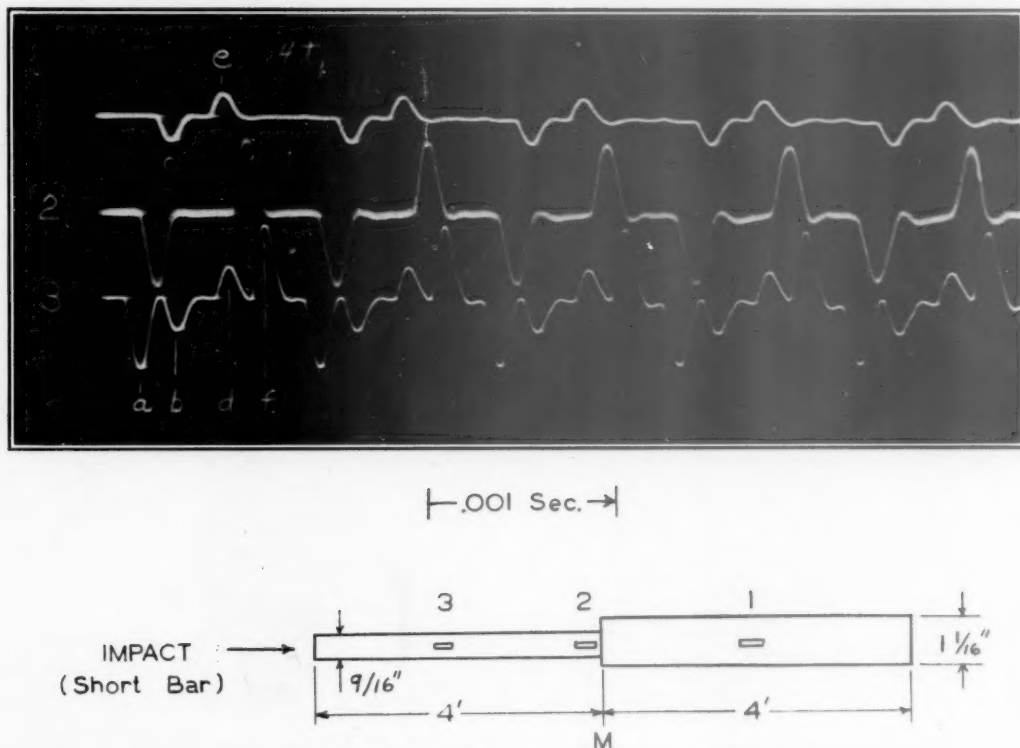


FIG. 9.—COMPLICATED COMPRESSION WAVE.

return of the compression wave from the small-diametered end. Fig. 10 shows these conditions in diagram form. This example illustrates the sort of analysis that may be made of the phenomena of strain-wave propagation and shows how complicated the picture becomes in any but simple cases. Fig. 11 shows the train of waves when the bar is struck from the large end. The gradual increasing complexity of the wave forms due to multiple reflection is characteristic of all such systems.

Fig. 12 shows the strain produced in a long steel bar by the impact on its end of a rifle bullet of 22 caliber. A circumferential gauge was used on the middle of the bar in order to measure the load produced in a very short gauge length. The initial pulse appears at *A*, and successive reflections at

faithfully reproduced in the wave traveling longitudinally until reflections occur from the open end.

We have good evidence, therefore, that the oscillographic records are faithful reproductions of high-frequency strain effect, and that the system of measurement is well suited for impact studies. Clark and Datweiler¹⁸ have reported results from a small pendulum tensile impact machine where the time-strain and time-stress relations were recorded on a cathode-ray oscillograph. Further work is in progress, but the entire program has been judged to be too intimately concerned with national defense to permit of present publication.

A good example of impact behavior is shown in Fig. 13, which represents a long,

slender knitting needle fired from a gun into a piece of wood. The needle is a column with very little lateral stiffness, but if the column is moved rapidly or supporting a load rapidly applied, the compression

caught in the photograph just before the needle stopped moving. Other needles are embedded in the wood with ends bent.

It is a matter of common experience that long slender nails may be successfully

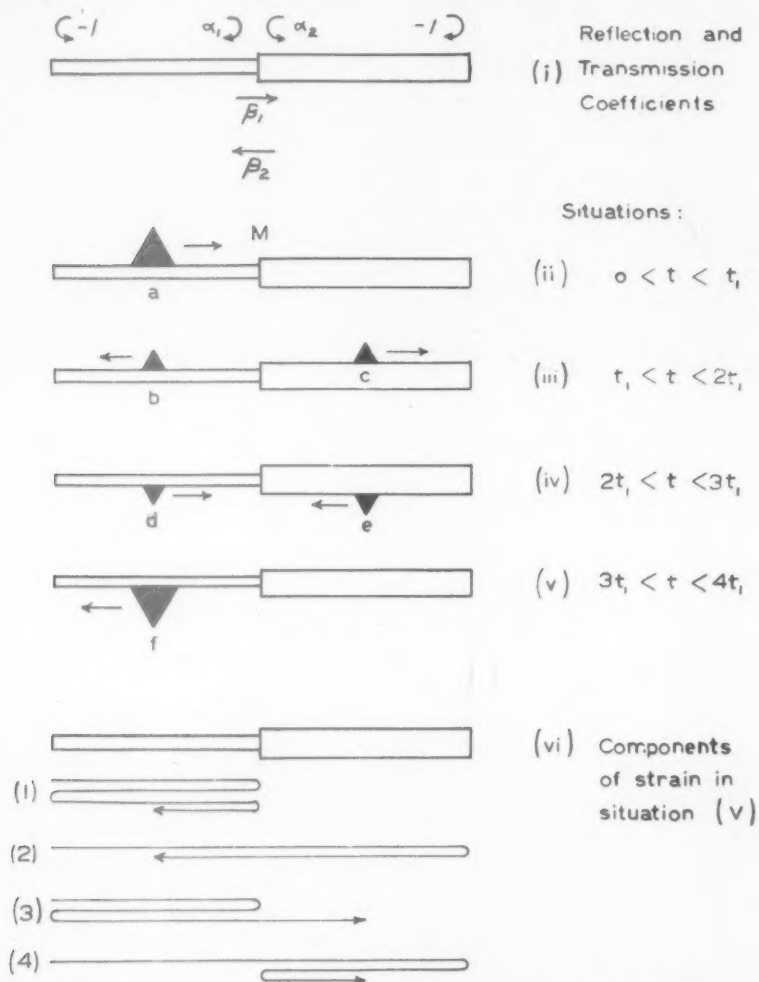


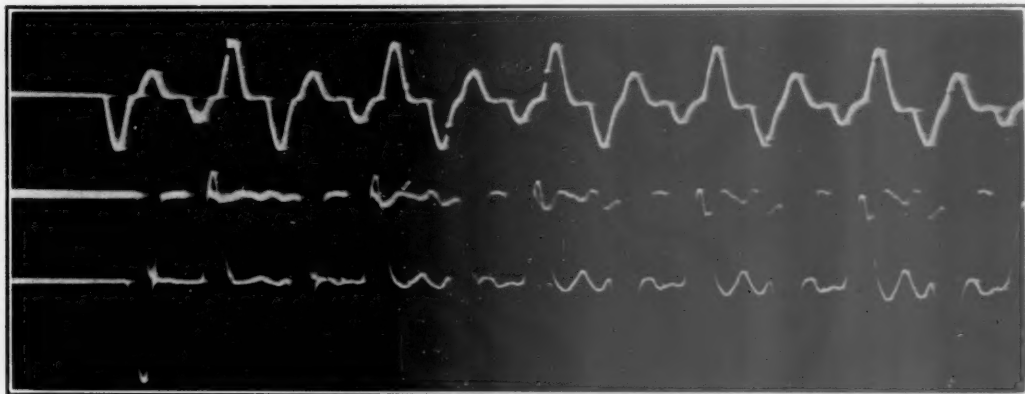
FIG. 10.—CONDITIONS OF COMPRESSION WAVE SHOWN IN FIG. 9.

member has no time in which to bend sideways and the column will withstand a load very far beyond the strength it could exhibit under slow loading. Fig. 14 shows the same knitting needle fired from a gun and photographed by Dr. Edgerton with his well-known high-speed flash illumination. After the slender needle has been sufficiently slowed down in traversing the wood, a speed is reached at which the wire has time to bend, and this behavior was

driven into a board by a rapidly moving light hammer when they cannot be made to penetrate under the impact of a slowly moving heavy hammer. The distance the nail will penetrate is also a very important function of the support of the board and it is equally well known that it may be impossible to drive a nail in an unsupported board without the expedient of placing another hammer below the board to provide an added rigidity, which

depends entirely on inertia effects. The same thing is even more evident in driving rivets. Here again is shown the important relation in all impact problems between the

the kinetic energy of the moving mass. This may take place by slowly damped vibrations, as when a clapper hits a bell, the energy finally disappearing by dissipation



0.001 Sec. →

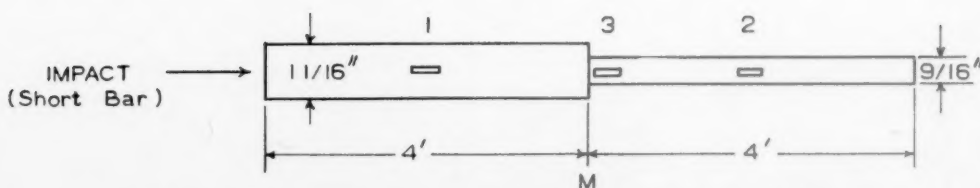


FIG. 11.—TRAIN OF WAVES WHEN BAR IS STRUCK FROM LARGE END.

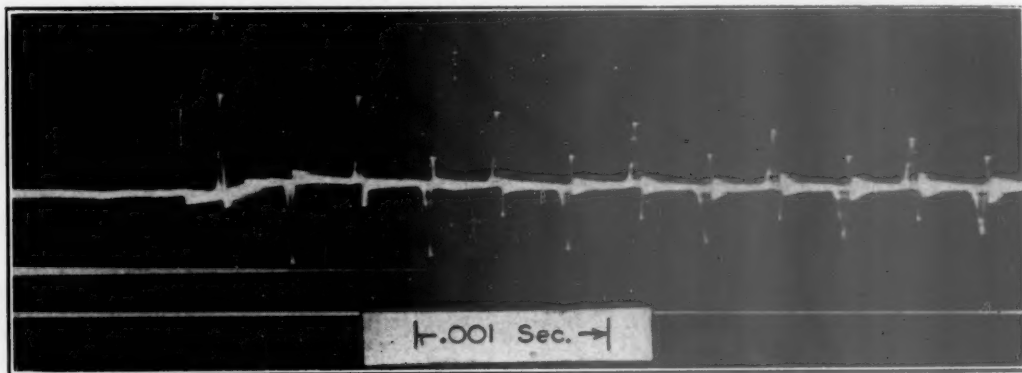


FIG. 12.—STRAIN PRODUCED IN LONG STEEL BAR BY IMPACT OF BULLET ON ITS END.

character of the load, the instantaneous distribution of stress and the dynamic reactions of the supporting structure.

PROBLEM OF IMPACT RESISTANCE

Essentially, the problem of impact resistance lies in the method of dissipating

as heat and sound waves; in overcoming static friction, as in the work of a pile driver; or by plastic deformation, as in forming metal under a drop hammer. In each case a certain amount of energy is dissipated as heat. In any impact involving actual structures, all three modes of dissi-

pation frequently appear, although in the case where repeated loads regularly occur, the work done in plastic deformation must be restricted.

pressures and the distribution of the impact energy over a longer length of time than to the loss of energy by deformation of the lead. A spring between the hammer and

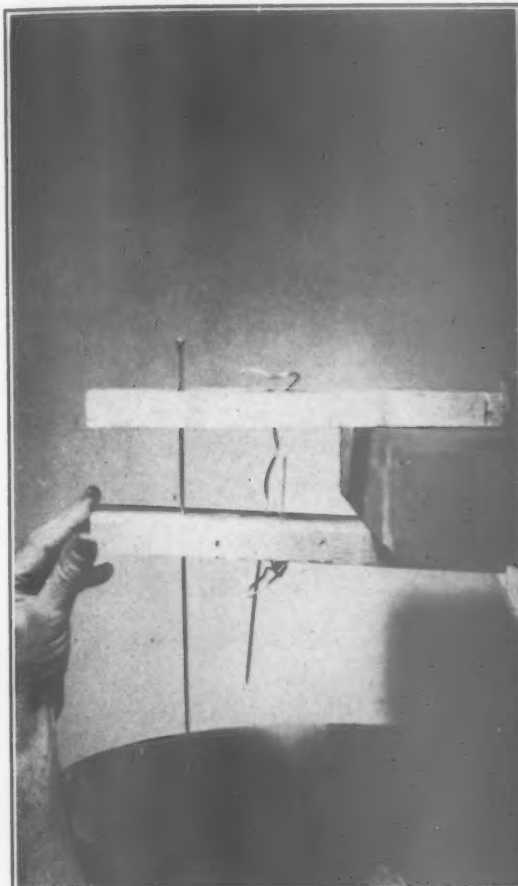


FIG. 13.—KNITTING NEEDLE FIRED INTO WOOD.

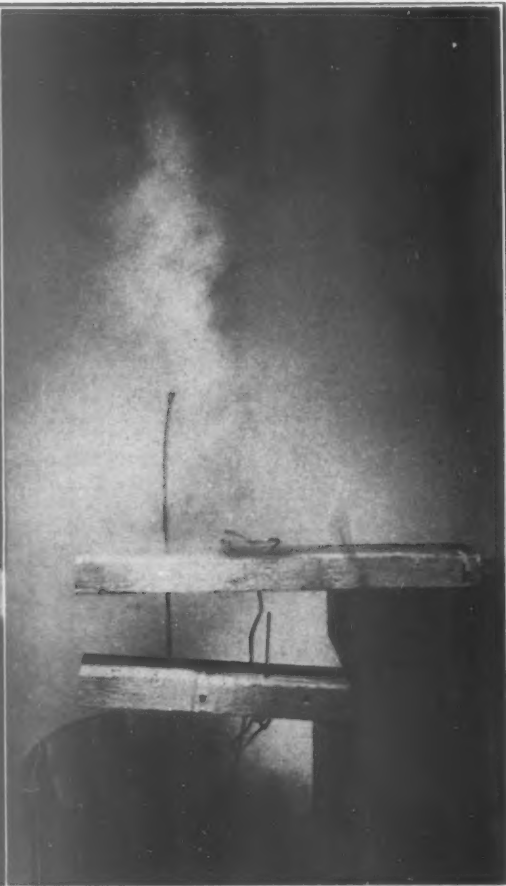


FIG. 14.—PHOTOGRAPH UNDER EDGERTON'S HIGH-SPEED FLASH ILLUMINATION OF A KNITTING NEEDLE FIRED INTO WOOD.

Whenever the energy is concentrated in such a way as to be absorbed in small volumes of material, extremely high pressures are built up over small areas and local breakdown occurs. For instance, a nail can be readily driven into a board with a steel hammer, but if the hammer is of lead the load concentration will result in plastic flow, thereby failing to build up a sufficiently high pressure to overcome the friction of the nail in the wood. In this case the different behavior of the nail is due more to the lowering of the peak

the nail would do the same thing, and constitutes the simplest "shock absorber."

Elastic deformation and rate of deflection under load then becomes of primary importance in questions of impact strength, quite apart from any inherent quality of the material from which the structure is formed. When loads are applied beyond the elastic limits that can be cared for by design, energy absorption by means of plastic deformation becomes of great importance. Here again, the paramount question is as to whether small sections

are constrained so as to hinder deformation, or whether yielding is safely distributed. The malevolent influence of notches, whether accidentally present from defects in materials or due to improper design, is of the same overwhelming importance as in the better known problem of fatigue strength. Here also, design is more fundamentally important than any inherent property of statically ductile metal.

COMBINED STRESSES

Finally comes the question of the characteristic "impact strength" as defined by Professor Howe, and it turns out that this illusive property can be reached only by studying combined stresses acting through the mechanism of notch constraint. It appears, therefore, that the greatest hope for future progress in the strength of materials phase of the problem lies in the direction of a simplification of combined stress testing. The general problem of designing structures to resist impact is mostly a question of stress-wave propagation, and in this field loads and their distribution depart so greatly from accepted methods of calculation that we may expect recent progress in the measurement of transient strains to prove of value.

IMPORTANCE OF STUDY

In closing this brief review, I can find no words more timely than those of Professor Howe, written in 1916: "The mechanism of deformation has been before us so little that a word as to its importance may not be remiss. The usefulness of steel really results from its resistance to deformation, and its power to endure limited plastic deformation. Hence a knowledge of the mechanism of this deformation and of the way in which steel in part resists deformation and in part accommodates itself to it, may in time disclose to us the essence of its power of resistance and accommodation. To understand this essence is to be the better prepared to approach the problem

of fitting the metal for its service to our race, not empirically alone, but also scientifically."

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Iron-ore Concentration and the Lake Erie Price

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(Pittsburgh Meeting, April 1940)

THE mysterious Lake Erie price for iron ore, established each spring, determines the maximum price that will be paid during the following season for ore of Mesabi Non-Bessemer base grade. This price is important to the ore producers, but since most of the ore in the Lake Superior district is owned or controlled by consuming interests, the really important question to them is not the price of ore but how much it will cost them to mine and transport their season's requirements to their furnace plants. However, a few million tons are actually sold each year, and considerable quantities are traded for mixing purposes, and the negotiations for these sales and trades usually begin with some reference to the Lake Erie price.

There is no difficulty with the Lake Erie price itself or with the manner in which it is established, but the system prescribed for determining the values of ores that are not exactly base grade is incomplete. The Lake Erie price takes into consideration only the iron and phosphorus contained in the ore, but when the ore producer is negotiating a sale or trade, he is confronted by the fact that his ore must be studied and the price adjusted, not only on the basis of the iron and phosphorus analyses, as specified by the Lake Erie price, but also on the basis of silica, alumina, manganese, structure, etc. The vague and unsatisfactory methods used in making these adjustments bear some relation to the

manner in which the ore is supposed to act in the blast furnace. The ore producer may not understand all of the idiosyncrasies of the blast furnace, but if the smelting-plant operators have a system more accurate than the Lake Erie price method for determining the relative values of different ores, why not pass this information on to the ore producers, so that they can make use of it and perhaps modify their practice in such a manner as to benefit both themselves and their customers? There is a lack of understanding and appreciation between these two groups that may, to some extent, be unavoidable, but in the interests of efficiency and conservation rules that are more accurate and complete than the Lake Erie price method in use at the present time should be established for the guidance of the ore producers.

Recently a paper was read before the Eastern States Blast Furnace and Coke Oven Association, by Mr. G. W. Hewitt, Manager Production, Blast Furnace and Coke Oven Department, Wheeling Steel Corporation, in which he explained how his company determines the relative values of different grades of Non-Bessemer ore. This is a very important paper, perhaps not so much on account of the actual calculation methods described as because of the fact that premiums and penalties are shown on Non-Bessemer ores for silica, alumina, phosphorus, and manganese. As pointed out by Mr. Hewitt, the premium and penalty system described may not apply without adjustments to other smelting plants. However, if the various ore

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consumers could get together and agree on a new set of rules for determining the relative values of different ores, it would be greatly to the advantage of the industry.

It is now generally accepted by producers and consumers of iron ore that the great iron and steel-producing industry along the Great Lakes must in the future secure more and more iron ore by concentrating the lean ores that exist in such enormous quantities in the Lake Superior district. At the present time, about one ton out of every five shipped from Minnesota is concentrate. Unless there is some new and entirely unforeseen development in the near future, such as the discovery of a new Mesabi Range, the production of concentrate from lean ores must increase in the future more rapidly than it has in the past.

FORMULA FOR DETERMINING GRADE OF CONCENTRATE

The ore producers that are attempting to develop this industry have many problems, but one of the most troublesome is the question of what grade of concentrate they should design their plants to produce in order to secure the greatest efficiency and economy. It should be understood that concentrate is a manufactured product, and the producer can frequently design his plant to produce ores varying widely in analysis and structure. Of course, it costs more to produce some grades than others, but at present the ore producer has no definite rule to guide him in determining the grade that will be of greatest value to the smelting plants. Whenever plans are being made for the construction of a new concentration plant, the characteristics of the various grades of ore that can be produced are accurately determined by elaborate experiments. Everyone understands that some of these characteristics are very important, but after the test results are all assembled, the real value of the various grades of concentrate cannot be determined, because the Lake Erie price is

determined by the iron and phosphorus contents only. In an endeavor to make possible the more efficient design and operation of concentration plants and provide a better basis for the trading of ores, a formula has been developed that may be used to determine more accurately the relative Mesabi Non-Bessemer values of ores delivered at lower Lake ports. This formula takes into consideration only the iron and gangue minerals in the ore, and does not take into account any of the other valuable or detrimental elements, but even this would be a great improvement over the present method, which recognizes definitely only the iron content of Non-Bessemer ore. For example, Mesabi Non-Bessemer ores of approximately 51.50 per cent Fe are being shipped, containing from 4.5 to 13.5 per cent SiO_2 . Obviously, the low-silica ore is the most valuable, although the Lake Erie price of both grades is the same (Table 1).

TABLE 1.—*Natural Analysis of Ore Used as Base Grade*

Constituent	5-year Weighted Average All Lake Ores, Per Cent	Suggested Base Ore, Per Cent
Fe.....	51.53	51.50
SiO_2	7.61	7.60
Al_2O_3		2.00
CaO		0.40
MgO		0.40

The formula presented for consideration in this paper may be stated in its simplest form as follows:

$$V = 0.11944U - 0.12774(A - \frac{1}{4}B)$$

in which

V = Mesabi Non-Bessemer Lower Lake Value of the ore when the price of base grade ore is \$4.95 per ton,

U = number of units of iron in the ore,

A = number of units of acids ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) in the ore,

B = number of units of bases ($\text{CaO} + \text{MgO}$) in the ore.

Examples

1. To determine the Mesabi Non-Bessemer value of an ore of the following natural analysis: Fe, 52.55 per cent; SiO_2 , 4.28; Al_2O_3 , 2.28; CaO, 0.25; MgO , 0.18;

$$V = 0.11944 \times 52.55 - 0.12774[(4.28 + 2.28) - \frac{1}{4}(0.25 + 0.18)]$$

$$V = 6.277 - 0.824 \quad \text{or} \quad \$5.453$$

The Lake Erie price of this ore is \$5.051.

2. To determine the Mesabi Non-Bessemer value of an ore of the following natural analysis: Fe, 50.73 per cent; SiO_2 , 7.12; Al_2O_3 , 2.49; CaO, 0.79; MgO , 0.30;

$$V = 0.11944 \times 50.73 - 0.12774[(7.12 + 2.49) - \frac{1}{4}(0.79 + 0.30)]$$

$$V = 6.059 - 1.193 \quad \text{or} \quad \$4.866$$

The Lake Erie price of this ore is \$4.876. The derivation of this formula is entirely mathematical, and does not involve any important approximations if the fundamentals have been accepted. These fundamentals and a discussion of the formula are presented, since, without them, the formula cannot be properly criticized.

DERIVATION OF FORMULA FOR MESABI NON-BESSEMER ORE VALUE

In a Bureau of Mines report in 1924, Read, Joseph and Royster¹ reach the conclusion that each unit of silica in the ore above 8 reduces the value by about 15¢ per ton. In a later report by the Bureau of Mines, T. L. Joseph² establishes the figure at about 13¢ per unit of SiO_2 . He quotes several investigators to show that theoretically 0.29 lb. of carbon is required "to decompose the limestone for one pound of slag and to melt the slag." This is a minimum, and certain additions must be made in actual practice. After studying the results of 45 blast furnaces, Joseph arrived at the conclusion that 0.4 lb. of coke is a "conservative figure for the coke equivalent of one pound of slag." Several other authors have written articles in which this

¹ References are at the end of the paper.

subject of ore values is discussed, and much information is available on the subject of blast-furnace operations. By the use of these publications and with the assistance of valuable information received from private sources, it has been possible to establish a method by which the average cost of pig iron produced from ore of any reasonable analysis can be computed. These calculations start with an itemization of the costs involved in producing pig iron in a 700-ton blast furnace from ore of a given analysis at Cleveland, Ohio, in 1938. The Lake Erie price of this ore is \$4.95 per ton, and using this ore, pig is produced at a cost of \$17.79 per ton. The assumption is then made that, other things being equal, if it costs more than \$17.79 to produce a ton of pig iron from another ore, this ore is worth less than \$4.95 per ton, and if pig can be produced from this ore for less than \$17.79, the ore is worth more than \$4.95 per ton. On this basis, smelting costs were computed for five ores all having the same iron analysis. The fact is recognized that the costs used may not be representative for any particular plant, but since all ores are compared on exactly the same basis, even fairly radical changes in basic operating costs will affect the comparisons only slightly, as will be shown later. The results of these calculations are shown in detail in Tables 2 and 3.

Table 2 shows in detail the various items of expense involved in producing pig iron at Cleveland from ore of the analysis shown in Table 3. It requires 1.664 tons of this ore at \$4.95 per ton to produce a ton of pig. In the smelting operation, 168 lb., or 0.075 ton of dust per ton of pig, is blown out of this ore, and must be sintered and returned to the furnace at a cost of \$1.50 per ton of sinter. Cinder, scale, and slag are added to the charge in the amounts shown, and limestone is added to flux all of the silica and alumina in the charge. The amount of coke required to smelt the ore is 0.875 ton, or 1750 lb. per ton of pig.

Adding together the cost of these raw materials gives a cost of \$13.93 per ton of pig. To this must be added various items \$2.35 for depreciation and fixed charges, and 96¢ for administration and selling expense. The total of all of these items gives

TABLE 2.—*Distribution of Smelting Costs*
Producing 700 Tons per Day Pig Iron at Cleveland, Ohio, in 1938

Item	Unit Cost	Quantity		Cost	
		Tons per Ton Pig	Tons per Day	Per Ton Pig	Per Day
Iron ore.....	\$4.95	1.664	1,164.75	\$8.236	\$5,765.51
Sintering flue dust.....	1.50	0.075	52.38	0.112	78.57
Cinder and scale.....	1.00	0.071	49.70	0.071	49.70
Basic slag.....	0.50	0.089	61.88	0.044	30.94
Limestone.....	1.25	0.350	244.04	0.437	305.05
Coke.....	5.75	0.875	612.50	5.03	3,521.88
Total raw materials.....				\$13.930	\$9,751.65
Total department labor.....				0.50	
Steam, blowing.....				0.35	
Miscellaneous steam, water and electricity.....				0.19	
Repair and maintenance materials.....				0.18	
Expense exhibits.....				0.19	
Relining fund.....				0.25	
Works general expense.....				0.10	
Pigging and handling.....				0.25	
Total operating cost above raw materials.....				\$2.01	
Credit surplus gas.....				1.46	
Total net operating cost above raw materials.....				\$0.55	
Depreciation and fixed charges.....				2.35	
Administration and selling.....				0.96	
Total cost above raw materials.....				\$3.86	2,700.00
Total cost.....				\$17.79	\$12,451.65

TABLE 3.—*Analyses of Furnace Charge and Products*

Constituent	Mesabi Non-Bessemer Ore Natural	Limestone	Cinder and Scale	Basic Slag	Coke
Fe, per cent.....	51.50	0.34	72.21	21.96	0.73
P, per cent.....	0.062	0.01		0.98	
Mn, per cent.....	0.35		0.29	14.48	
SiO ₂ , per cent.....	6.60	2.00		20.94	4.00
Al ₂ O ₃ , per cent.....	1.76	0.50		3.24	1.44
CaO, per cent.....	0.18	51.00		18.90	1.60
MgO, per cent.....	0.18	3.50		6.93	0.16
S, per cent.....		0.08	0.035	0.12	0.42
Ignition loss.....	4.40				
Moisture, per cent.....	12.00				3.65
Fixed carbon, per cent.....					88.00
Pig Iron Composition, Per Cent		Slag Composition, Per Cent			
C.....	4.25	SiO ₂	35.86		
Mn.....	1.47	Al ₂ O ₃	10.68		
Si.....	0.80	CaO.....	45.25		
S.....	0.05	MgO.....	4.93		
P.....	0.22	MnO.....	1.47		
Fe.....	93.21	FeO.....	1.03		
		S.....	0.78		

of operating expense, and the credit for surplus blast-furnace gas must be deducted. This gives a total net operating cost above raw materials of 55¢ per ton of pig iron. To this must be added the large item of

the cost of producing and selling the pig as \$17.79 per ton.

The charge of \$2.35 per ton for depreciation and fixed charges is the major item of expense, excepting only the cost of the

raw materials. A 700-ton furnace plant operating at full capacity for a year will produce a maximum of 255,500 tons of pig, and at \$2.35 per ton this amounts to slightly over \$600,000 per year for depreciation and fixed charges. A 700-ton furnace plant will cost approximately five million dollars. If this is depreciated at a rate of 5 per cent per year, and interest at 5 per cent is paid on the investment, these two items amount to 10 per cent of the investment, or \$500,000 per year, leaving only \$100,000 per year for taxes, insurance, et cetera.

The administration and selling expense of 96¢ per ton, or approximately \$250,000 per year, maintains the offices and pays the salaries of all the officers of the company, including the purchasing staff and the sales organization. The cost of maintaining the sales organization alone, according to the U. S. Tariff Commission Report No. 23, of June 16, 1931, amounts to 27¢ per ton, or approximately \$70,000 per year.

It should be noted that the cost of the pig is computed on the basis of operating at 100 per cent capacity for 100 per cent of the time. If the furnace is shut down for any reason, many of the fixed charges continue; therefore the average cost of the pig produced from the ore may be considerably above the figure shown. However, since all costs are to be compared on the same basis, operating time is not considered in these calculations.

In order to apply the costs in Table 2 to ores of other grades, certain assumptions and generalizations were made. It required 1.664 tons of ore assaying 51.50 per cent nat. Fe to produce one ton of pig in the original calculations. This means that 85.7 iron units are supplied by the ore for each ton of pig produced. This figure of 85.7 is considered to be a constant for all ores, and, therefore, if an ore assays only 50 per cent nat. Fe, 1.714 tons will be required per ton of pig. The rest of the iron in the pig comes from the other con-

stituents of the charge; namely, the cinder, scale, and basic slag, and the amount of these constituents is held constant at 0.16 ton per ton of pig, regardless of the type of ore being smelted.

The amount of flue dust sintered when smelting the original ore was approximately 4.5 per cent of the weight of the ore. This figure was kept constant for all other ores. Later, the subject of ore structure will be discussed in more detail, but in comparing smelting costs all ores were considered to have the same structure, and, therefore, produce the same percentage of dust to be sintered.

The amount of limestone to be added is computed for each ore to be sufficient to produce a neutral slag, considering all of the silica and alumina in the charge as acids. Since a portion of the silica will appear as silicon in the pig iron, the actual furnace slag that will be produced will be slightly basic.

The amount of coke required for the original ore was 1750 lb. per ton of pig, or 612.50 tons per day. With all ores, the furnace is assumed to burn 612.50 tons of coke per day. This means that the same amount of air will be blown into the furnace at the same blowing cost, and approximately the same amount of gas will be produced regardless of the analysis of the ore. These 612.50 tons of coke smelt 1164.75 tons of the original ore, from which are produced 700 tons of pig per day and 956 lb. of slag per ton of pig. Sulphur elimination is not considered, but it is assumed that sufficient slag will be made to keep the sulphur below 2 per cent. For each additional pound of slag produced from any other ore, 0.4 lb. of coke is required, and since the furnace burns 612.50 tons of coke per day, less ore can be smelted and less pig produced if the slag volume increases above 956 lb. Conversely, if the slag volume decreases below 956 lb., a greater amount of ore can be smelted and a greater tonnage of pig iron can be

produced. By these means, it is possible to compute the number of tons of pig the furnace will produce per day from any given ore, and also to determine the total cost per day of all raw materials.

Table 4 shows the detailed calculations made for five different Mesabi Non-Bessemer ores, all having the same natural iron analysis. It will be observed that the number of tons of pig produced per day

TABLE 4.—*Comparison of Smelting Costs*
Mesabi Non-Bessemer Ores, 51.50 Per Cent Fe

Ore No.	1	2	3	4	5
Analysis, Natural, Per Cent:					
Fe.....	51.50	51.50	51.50	51.50	51.50
P.....	0.062	0.071	0.068	0.051	0.072
Mn.....	0.35	0.40	0.36	0.52	0.48
SiO ₂	6.60	5.16	6.93	9.02	11.93
Al ₂ O ₃	1.76	2.28	2.55	1.74	1.12
CaO.....	0.18	0.25	0.12	0.14	0.23
MgO.....	0.18	0.18	0.11	0.12	0.13
Ignition loss.....	4.40	4.92	2.76	3.77	4.57
Moisture.....	12.00	12.16	12.92	10.32	7.01
Tons ore per day.....	1,164.75	1,185.20	1,140.61	1,114.51	1,070.68
Tons stone per day.....	244.04	222.29	270.59	295.40	335.99
Tons sinter per day.....	52.38	53.33	51.33	50.15	48.18
Tons scale, etc., per day.....	112.00	113.96	109.67	107.16	102.95
Tons pig per day.....	700.00	712.26	685.46	669.78	643.44
Pounds slag per ton pig.....	956.00	880.48	1,048.14	1,152.75	1,339.72
Cost of ore per day.....	\$5,765.51	\$5,866.74	\$5,646.02	\$5,516.82	\$5,299.87
Cost of coke per day.....	3,521.88	3,521.88	3,521.88	3,521.88	3,521.88
Cost of stone per day.....	305.05	277.86	338.24	369.25	419.99
Cost of scale, etc., per day.....	80.64	82.05	78.96	77.16	74.12
Cost of sinter per day.....	78.57	80.00	77.00	75.22	72.27
Total cost per day above raw materials.....	2,700.00	2,700.00	2,700.00	2,700.00	2,700.00
Total cost per day.....	\$12,451.65	\$12,528.53	\$12,362.10	\$12,260.33	\$12,088.13
Cost per ton pig.....	\$17.789	\$17.590	\$18.035	\$18.305	\$18.787
Difference per ton pig.....	0	+0.199	-0.264	-0.516	-0.998
Difference per ton ore.....	0	+0.120	-0.148	-0.310	-0.600
Ore value at Cleveland.....	\$4.950	\$5.070	\$4.802	\$4.640	\$4.350
Lake Erie price.....	4.95	4.95	4.95	4.95	4.95

The total cost above raw materials, as shown in Table 2, is \$2700 per day. Since the furnace will be burning the same amount of coke, requiring the same amount of air and producing approximately the same amount of gas each day, the total operating costs and the credit for surplus gas will be approximately the same each day. The cost per day of pigging and handling will vary only slightly with minor changes in the amount of pig produced, and depreciation and administrative expenses will be constant. Then the total cost above raw materials will be approximately the same each day, regardless of the grade of ore being smelted. In these calculations, this cost was held constant at \$2700 per day.

varies from 712.26 tons with the No. 2 ore to 643.44 tons with the No. 5 ore. This change is due entirely to the change in the volume of slag produced, which varies from 880.48 lb. for the No. 2 ore to 1339.72 lb. for the No. 5 ore. These changes affect the cost of producing the pig iron, which varies from \$17.59 per ton with the No. 2 ore to \$18.79 per ton with the No. 5 ore. This difference in the cost of the pig is due entirely to the difference in the analysis of the ore, and, therefore, if the No. 1 ore has a value of \$4.95 per ton, No. 2 ore is worth \$5.070 per ton, and No. 5 ore is worth only \$4.350 per ton. However, the Lake Erie price of all of these ores is the same. Obviously, the Lake Erie price is relatively too high for the No. 5 ore and

too low for the No. 2 ore. The difference is even greater than is shown here from the standpoint of profit, if any is being made by the smelter, because the furnace will produce a greater tonnage of pig per day from No. 2 ore.

THE GENERAL FORMULA

From this analysis, it is evident that if these cost figures and the other operating conditions are accepted, a definite mathematical relation can be set up by which the relative values of different Mesabi Non-Bessemer ores may be computed. Such a formula was derived and, after being simplified, took the following form:

$$\frac{V}{U} = \frac{P'}{U'} + K(F' - F) \quad [1]$$

in which

K = a constant determined by the cost of coke, stone, labor, overhead, etc., at the blast furnace, and, for the data shown = \$0.12774

P' = base price of Mesabi Non-Bessemer ore, in recent years = \$4.95

V = Mesabi Non-Bessemer value of the ore in question

U' = iron units in base ore = 51.50

U = iron units in the ore in question

F' = ore factor of base ore

F = ore factor of ore in question

$\frac{V}{U}$ = unit value of the ore in question

$\frac{P'}{U'}$ = base unit price of the Mesabi Non-Bessemer ore = \$0.09612

$F = \frac{A - \frac{1}{4}B}{U}$ for any ore, in which

A = total acids, $\text{SiO}_2 + \text{Al}_2\text{O}_3$

B = total bases, $\text{CaO} + \text{MgO}$

$$F' = \frac{A' - \frac{1}{4}B'}{U'} = \frac{9.60 - \frac{1}{4}(0.80)}{51.5} =$$

0.18252, for the base ore shown in Table 1. Then, by substituting in the general formula 1,

$$\frac{V}{U} = \frac{4.95}{51.5} + 0.12774(0.18252 - F) \quad [2]$$

or

$$\frac{V}{U} = 0.11944 - 0.12774F \quad [3]$$

which is the 1938 unit value of the ore in question,

$$V = U(0.11944 - 0.12774F) \quad [4]$$

which is the 1938 value of the ore in question, but

$$F = \frac{A - \frac{1}{4}B}{U}$$

and, therefore,

$$V = 0.11944U - 0.12774(A - \frac{1}{4}B) \quad [5]$$

The general formula, No. 1, shows that the unit value of an ore is equal to the base unit price plus a constant times the difference between the base ore factor and the ore factor of the ore in question. With the price and analysis of the base ore established, the only variable in the formula is F , the ore factor of the ore in question. Then, the ore factor of an ore really determines its unit value, and since F is a negative factor, the smaller the ore factor, the higher the unit value of the ore. This formula may be written $V = U\left(\frac{P'}{U'}\right) + UKF' - UKF$. This shows that the value of an ore of iron content U is determined by the term $(-UKF)$, but $F = \frac{A - \frac{1}{4}B}{U}$, and, therefore, this last term becomes $-K(A - \frac{1}{4}B)$, or $-0.128A + 0.032B$. This shows that the value of the ore decreases 12.8¢ for each unit of silica plus alumina that it contains, and increases 3.2¢ for each unit of base that it contains (Joseph estimates 13¢ per unit of silica). The credit of 3.2¢ per unit of base is due to the fact that the more base in the ore, the less limestone must be provided by the blast-furnace operator. A unit of base in the form of limestone costs the blast-furnace operator 2.6¢, while a unit of base in the ore costs him nothing.

In addition to this, a unit of base in the limestone carries with it about $\frac{1}{20}$ of a unit of silica, which at 12.8¢ per unit is about 0.6¢ additional, making a total of 3.2¢ increase in value for each unit of base in the ore.

The constant K in the formula will change very slightly from year to year as blast-furnace operating costs and the costs of raw materials change. This constant depends primarily upon the assumption made in computing the cost of producing pig iron and in deriving the general formula, that 0.4 lb. of coke is required to "decompose the limestone for one pound of slag and to melt the slag." This figure, in the opinion of the experts, is a close approximation of the actual increase, and will, of course, not change from year to year. Therefore, the constant $K = \$0.12774$ will not change materially unless there is a major change in blast-furnace practice or in the cost of stone or coke. For example, an increase of \$1.00 per ton in the cost of coke would change this factor to 0.13757. An increase of \$0.50 per ton in the cost of limestone would change the factor to 0.13850. An increase of \$1000 per day in operating cost would change the factor to 0.14380. There is plenty of room for argument in determining this constant, but from the information available it seems that a good average would be between 0.12 and 0.13.

APPLICATION OF FORMULA

Using formula 5, the Non-Bessemer values of 30 ores shipped from the Mesabi Range in 1938 were computed (Table 5). In this table the ore factors are shown and the ores are listed in the order of increasing ore factors. The table also shows the iron unit value of each ore, and it is evident that ores having ore factors below 0.18252 have iron unit values above the Lake Erie iron unit price, and ores having ore factors above the base ore factor have unit values below the Lake Erie iron unit

price. In this table are also shown the values computed according to the method described by Mr. Hewitt in the paper referred to previously. These values include only the iron unit value, the gangue premium or penalty, and the freight disadvantage shown by Mr. Hewitt, but do not include premiums or penalties for phosphorus, manganese, or alumina-silica ratio. It should be understood that Mr. Hewitt uses an ore of a different analysis as his base, and in addition to this, his method computes the Lake Erie value of the ore for his smelting plant, which is near the Pittsburgh district. Smelting costs at that plant are very different from costs at Cleveland, since there is an additional freight charge against Mr. Hewitt's plant of \$1.14 per ton, and since coke at this plant costs \$2.70 per ton and at Cleveland \$5.75 per ton. Regardless of these great differences, the values of the ores shown in Table 5 computed by the formula check quite closely in most instances with the values computed by Mr. Hewitt for his inland furnace plant. The ore used by Mr. Hewitt as his base grade has an ore factor of 0.17869, as compared with 0.18252 used by this author, and Mr. Hewitt uses a gangue penalty of 10.1¢ per unit, which compares roughly with the constant $K = \$0.12774$, or 12.8¢ used by this author. Both methods agree in showing that the value of ore that is better than base grade is higher than the Lake Erie price indicates, and the value of ore that is poorer than base grade is lower than the Lake Erie price indicates.

PREMIUMS

This formula gives the Mesabi Non-Bessemer value of any ore. For Bessemer and Old Range ores, the normal premiums must be added before comparisons can be made with Lake Erie prices. Whether or not the premiums now used for Bessemer and Old Range ores accurately indicate the increases in value is a question for the

smelting-plant operators to decide. The ore producers would be very much interested in an open discussion of this question. In the paper by Mr. Hewitt previously referred to, the author states that he considers Old Range ores worth 3¢ more than the 15¢ premium now in use. If this

ORE VALUES AND CONCENTRATION

If ores were sold, traded, or transferred on the basis of computed values rather than on the basis of Lake Erie prices, the blast-furnace operator would not be affected, because the formula adjusts values so that pig iron can be made from all ores

TABLE 5.—*Comparison of Lake Erie Price and Ore Values*
Mesabi Ores Shipped in 1938

Ore No.	Fe (Nat.), Per Cent	Lake Erie Mesabi Non-Bessemer Price	Lake Erie Mesabi Non-Bessemer Value	Percentage of Value to Price	Ore Factor	Lake Erie Mesabi Non-Bessemer Unit Value	Hewitt Lake Erie Mesabi Non-Bessemer Value
1	57.54	\$5.531	\$6.293	113.78	0.0789	\$0.10936	\$6.177
2	55.31	5.316	5.768	108.50	0.1186	0.10429	5.708
3	52.55	5.051	5.453	107.96	0.1227	0.10377	5.361
4	54.35	5.224	5.613	107.45	0.1266	0.10327	5.545
5	53.99	5.190	5.387	103.80	0.1539	0.09978	5.358
6	48.70	4.602	4.932	107.17	0.1581	0.09924	4.748
7	52.18	5.016	5.137	102.41	0.1644	0.09844	5.109
8	53.73	5.165	5.273	102.09	0.1668	0.09813	5.261
9	52.23	5.020	5.110	101.79	0.1691	0.09784	5.069
10	52.68	5.064	5.123	101.17	0.1737	0.09725	5.107
11	49.91	4.797	4.851	101.13	0.1741	0.09720	4.778
12	51.60	4.960	5.008	100.97	0.1752	0.09706	4.987
13	53.07	5.101	5.111	100.20	0.1811	0.09631	5.106
14	49.61	4.754	4.777	100.48	0.1812	0.09629	4.725
15 ^a	51.50	4.950	4.950	100.00	0.1825	0.09612	5.005
16	54.45	5.234	5.232	99.96	0.1829	0.09608	5.260
17	53.87	5.178	5.169	99.83	0.1838	0.09596	5.195
18	53.94	5.185	5.144	99.21	0.1885	0.09536	5.170
19	52.93	5.088	5.038	99.02	0.1890	0.09518	5.053
20	51.95	4.993	4.937	98.88	0.1911	0.09503	4.973
21	52.68	5.064	4.994	98.62	0.1929	0.09480	5.008
22	53.31	5.124	5.044	98.44	0.1943	0.09462	5.075
23	53.56	5.148	5.026	97.63	0.2005	0.09383	5.074
24	52.75	5.070	4.943	97.50	0.2015	0.09370	4.970
25	53.27	5.120	4.982	97.30	0.2031	0.09350	4.955
26	50.55	4.859	4.707	96.87	0.2061	0.09311	4.701
27	49.56	4.747	4.560	96.06	0.2147	0.09201	4.521
28	49.00	4.660	4.475	96.03	0.2202	0.09131	4.453
29	50.86	4.889	4.496	91.96	0.2430	0.08840	4.520
30	47.72	4.414	4.188	94.88	0.2479	0.08777	4.148

^a Base grade.

is the experience of other smelting-plant operators, the ore producers would like to know just what characteristic of Old Range ore accounts for this large increase in value. It would seem that wash or jig concentrates are at least the equal of Old Range ores in structure, and yet the present system penalizes them 15¢ per ton. Hot abrasion and reducibility tests on various iron ores have been made by the Bureau of Mines,^{3,4} and there appears to be nothing in their studies to indicate that Old Range ores, as such, should arbitrarily receive any premium at all, although no complete comparison was made.

at the same smelting cost. Only a change in the cost of base ore would affect blast-furnace costs. However, the change from price to value would have considerable effect on the ore producer, especially on the producer of concentrate from low-grade ore. Consider an operator who has 10,000 tons of Mesabi ore to sell, assaying 51 per cent Fe and 13 per cent SiO₂, neglecting the other constituents. The Lake Erie price of this ore would be \$49,021. If he removed 5 units, or 112 lb., of silica from each ton of ore, he would have left 9500 tons of ore assaying 53.68 per cent Fe and 8.42 per cent SiO₂, the Lake Erie price of

which would be \$49,021, exactly the same as though the silica had not been removed. The ore producer would have saved the freight on 500 tons of ore, or \$955, but probably this would not be sufficient to pay him for the expense of operating the plant to remove the silica. If this same ore were sold at its value at Lower Lake ports, the 10,000 tons of 51 per cent Fe ore would be worth only \$44,309, but the 9500 tons of 53.68 per cent Fe ore would be worth \$50,692, or an increase of \$6383, to which the saving in freight of \$955 is added, making a total difference of \$7338. This probably would be considerably more than the expense of operating the machinery to remove the silica, since it would amount to \$0.73 per ton of original ore. This example shows that with the present method of computing ore prices there is no economy in concentrating this ore, but if the ore were sold at its value, it would in all probability be concentrated before shipment, and the smelting-plant operators would produce less slag and more pig per day without affecting their costs per ton.

In the above example, it was assumed that the concentrating operation removed 5 units of silica, but otherwise did not change the ore. This, of course, never happens in any concentrating plant, because, among other elements, a certain amount of iron is always lost. It is possible, however, to apply this method of profit calculation to definite concentrating problems. Consider a concentrating operation in which the operator is to produce 100,000 tons of concentrate during a season, guaranteed to contain not less than 51.5 per cent natural Fe, and to be paid for at the Lake Erie price. The total cost of mining and concentrating this ore is \$2 per ton of crude. The operator can produce concentrate assaying 51.5 per cent natural Fe and 12 per cent SiO_2 , with a recovery of 75 per cent, or by simply changing the amount of wash water he is using he can produce concentrate assaying 54.50 per cent natural

Fe and 8 per cent SiO_2 , with a recovery of 66.6 per cent. The question is—which grade of concentrate should be produced in order to make the season's operation most profitable? If he produces 51.50 per cent Fe concentrate, he must mine and concentrate 133,333 tons of crude at a cost of \$266,667. He receives \$4.95 less the freight, or \$3.04 per ton, for the concentrate at the plant, which is a total of \$304,000 for the season, leaving him a profit of \$37,333. If he produces 54.50 per cent natural Fe concentrate, he must mine and concentrate 150,000 tons of ore at a cost of \$300,000. He receives \$5.24 less the freight, or \$3.33 per ton, for the concentrate, or \$333,000, which leaves him a profit of \$33,000 for the season. This indicates that the operator makes more profit by producing the lower grade of concentrate. However, if he sold his 51.50 per cent Fe concentrate at its value, he would receive \$4.62 less the freight, or \$2.71 per ton of concentrate at the plant. This is a total for the season of \$271,000, against an operating cost of \$266,667, which would mean a profit of \$4333. If he produced the higher grade of concentrate, however, it would have a value of \$5.49 less the freight, or \$3.58 per ton, which is \$358,000 for the season. Since his total cost is \$300,000, his profit for the season is \$58,000. This again indicates that if the ore were sold at its value, he would make a greater profit by producing the higher grade of concentrate, and his customer would have the advantage of being able to produce more tons of pig per day.

The concentrating characteristic curves of an iron ore are ordinarily plotted between weight recovery and iron assay of the concentrate that can be produced. In order to more definitely indicate the value of the concentrate, the ore factor also may be plotted against the concentrate recovery. Then, by the use of formula 4, $V = U(0.11944 - 0.12774F)$, the curve of value against concentrate recovery can be

drawn. If the curve showing the total cost of producing the various grades of concentrate is plotted on this same sheet, a curve showing the profit per ton can then

desirable for the operator to produce a higher grade product.

The curves in Fig. No. 2 are for an ore that is being concentrated by a consuming

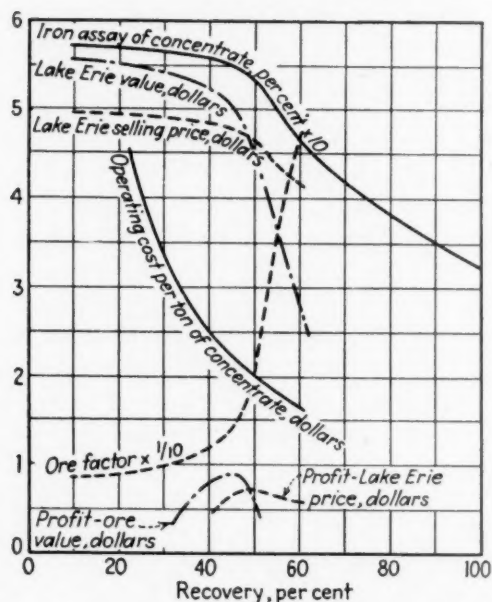


FIG. 1.—PROFIT AND CHARACTERISTIC CURVE, MESABI ORE.

be shown. Such a series of curves has been drawn for two different ores, as shown in Figs. 1 and 2. On these curve sheets are also shown the present selling price of the concentrate and the present profit per ton.

The ore shown in Fig. 1 is being used to fill a contract specifying that the natural Fe in the shipping product shall not be less than 51.50 per cent, and that the sales price shall be 85 per cent of the Lake Erie price less the freight. (Discounting the Lake Erie price is quite usual in actual sales by independent producers.) The curves show that a maximum profit of \$0.74 per ton of concentrate can be made when producing a 53.61 per cent natural Fe concentrate. However, if the ore is sold at 85 per cent of its value, a maximum profit of \$0.90 per ton of concentrate can be secured with 55.00 per cent natural Fe. This again indicates that the change from price to value in selling concentrate would make it

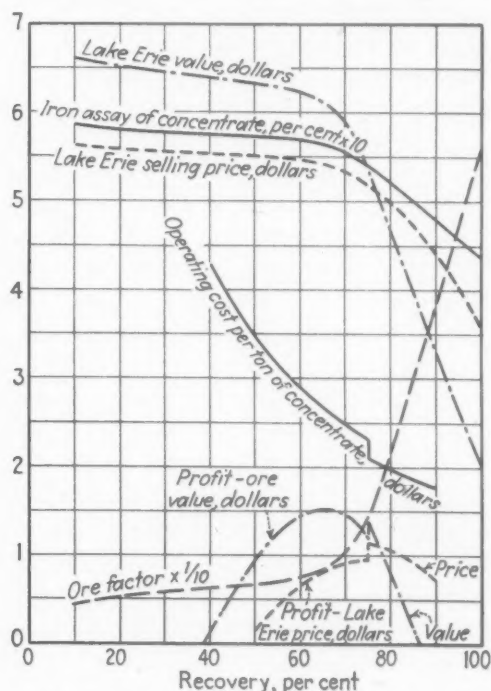


FIG. 2.—PROFIT AND CHARACTERISTIC CURVE, MESABI ORE.

interest, therefore the Lake Erie selling price is of no real importance. At the present time the ore is being washed, producing concentrate assaying 54.15 per cent natural Fe. The profit, based on the ore value, is \$1.40 per ton of concentrate. An increase in the grade of concentrate above 54.15 per cent Fe requires additional equipment in the concentrating plant and, therefore, additional operating expense. However, the curve shows that the maximum profit based on ore value would be secured by raising the grade of concentrate to 56.40 per cent Fe, giving a profit of \$1.53 per ton of concentrate. The maximum profit based on the Lake Erie price is \$1.16 per ton with a concentrate assaying 54.15 per cent Fe.

Profit calculations made on other ores sometimes show that a shift in ore selling

from price to value would reduce the apparent profit to the ore producers, but with all ores investigated, this shift would make it necessary for the producer to raise the grade of the concentrate he is shipping in order to secure maximum profit.

CONCLUSIONS

A simple formula has been developed, by the use of which the Mesabi Non-Bessemer value of any ore can be determined relative to the price of base ore. This formula was developed on the basis of giving values to all ores such that pig iron could be produced from any of them at the same price per ton. Two requirements are necessary before this formula will give accurate values: (1) base-grade ore must be completely defined, and (2) the added cost to the blast-furnace plant of smelting an ore containing an additional unit of silica plus alumina must be determined. An attempt has been made to satisfy both of these requirements, but if the figures suggested are not acceptable, new values can be substituted in the general formula and a simple expression secured, having new constants. The formula can also be modified to satisfy changes in base ore prices.

The use of this formula with the proper constants, replacing the Lake Erie price method now in use, will be a benefit both to the producers of concentrate and to the blast-furnace operators. The concentration-plant operators would find it desirable and often to their financial advantage to raise the grade of the concentrate they are producing, and the blast-furnace operator would get the benefit of greater furnace capacities, with no additional expense per ton of pig. In other words, an accurate method for determining ore values would result in better over-all economy from ore to pig iron. For any large consuming interest producing a variety of ores that, when mixed together, are about base grade, the transfer of ore

from the producing organization to the consuming organization on the basis of value rather than price would have little effect on the apparent income for the season, although the values of the ores produced from individual properties might differ radically from the Lake Erie prices.

The chief advantage of this change from price to value lies in the effect that such a change would make in concentration practice. The concentrates being produced by many of the plants now in operation are so low in grade that they must be mixed with low-silica ores before they can be smelted economically. As the low-silica ores controlled by any producing organization are exhausted and it becomes necessary to raise the grade of the concentrates that they are producing, the operation of their concentration plants will become less and less profitable, unless ores are sold or transferred at their actual values rather than at the prices computed by present methods. The future of the Lake Superior mining district and, to a large extent, the iron and steel industry of this country, depends upon the development of adequate facilities for producing concentrates of at least base grade from the enormous quantity of low-grade ore that is available. Unless the ore producers are credited with the full value of the product they ship, concentration operations will become less profitable in the future when it becomes necessary to produce higher grade concentrate.

Any discussion of iron-ore prices or values invariably brings up the question, in Minnesota at least, of the possible effect on taxes. The average ore shipped from the state is about base grade, or 51.50 per cent Fe. Since the proposed change from price to value would not change the selling price of base-grade ore, the average value of the ore shipped from the state would not be changed. For this reason, the total amount of money collected from the mining companies by the occupation tax would not

change, although the tax paid on any particular operation might be affected. The ad valorem tax is assessed against the value of the ore remaining in the ground. The analysis of the remaining ore is not known accurately, but if the analysis of the ore that has already been mined can be taken as an indication, the remaining ore will also assay about 51.50 per cent Fe. If this is true, a change from price to value in selling ore would have no effect on the total ad valorem tax paid by the mining companies, although the tax paid on any particular property might be affected.

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DISCUSSION

(C. L. Wyman presiding)

G. W. HEWITT,* Wheeling, W. Va.—In Mr. Davis' very able paper he has made a distinct contribution toward simplifying the calculation of ore values from analysis. In a brief formula, he summarizes the debit against silica and alumina (taking into account lime and magnesia) and bases the calculation on definite operating data at a consuming furnace at Cleveland.

We made somewhat similar studies of comparative ore values based on operating practice at an inland furnace plant in the Steubenville, Ohio, district and reported them in a paper to which Mr. Davis refers (see p. 30). The statement was made in that paper that total gangue could not be considered as a debit, that a certain amount was needed to furnish the slag volume required to take care of the sulphur in the coke and obtain smooth furnace travel. In other words, we must ask the consuming furnace operator to give us a definite standard gangue content of the ore

below which he loses in practice by going and above which we may calculate a debit per unit of gangue in having to supply coke, limestone and so on to take care of excess slag over the standard volume on which he gets his best practice. From this viewpoint, we stated that the calculation of ore values from analysis must properly be made for each consuming plant, based on the individual conditions.

In this connection, we must make it clear that our calculation on gangue debits made in the 1939 paper does not allow an interpretation such as if 5 per cent gangue costs so much to take care of in the blast furnace, 10 per cent gangue costs twice as much and 15 per cent three times as much. Rather our thought was as follows: At one certain consuming point, we want a standard gangue in the ore for best furnace practice; in this case, 9.3 per cent. If the gangue in a proposed ore goes over that figure we give each 1 per cent of excess a debit calculated from the operating conditions prevalent at that time, but do this only if our total ore burden to be used then averages over 9.3 per cent. In the same way, we give each 1 per cent gangue under 9.3 per cent on the proposed ore a credit, only if the average gangue in the total ore burden *does not go under 9.3 per cent*. And we would emphasize the point that the 10.1¢ per unit of gangue credit or debit applies only under capacity operating conditions and is considerably lessened under other operating conditions.

A good example of varying standard gangue requirements is found in our own company. We do not have the same standard or best practice slag volume at a lower Ohio River plant, where the coke runs 7.6 per cent ash and 0.50 per cent sulphur, as we have at an upper Ohio River plant, where the coke is 10.8 per cent ash and 1.02 per cent sulphur; consequently, we use different standards at the two points. Nor can we ignore the difference in freight cost from Lake Erie. We must include that in our calculation, because we pay 23 per cent more freight to the southern Ohio plant, and, other things being equal, an iron unit in an ore of higher iron content is worth more to us when the ore is delivered at the farther point than at the nearer.

The calculation covering gangue content in an ore is usually the most important detail, but in many ores the phosphorus must be taken

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into account. We are not thinking of Bessemer ores in this connection, as there is an established differential on these. But in our practice we have found that an increase in phosphorus in our non-Bessemer ores increases the cost of our burden in limiting the recovery of valuable metallics and excess lime from open-hearth slag, and this must be considered in determining comparative values of ores.

Mr. Davis is especially interested in his paper in the problem of determining whether any particular concentrating or beneficiating operation pays for itself. We have found such a problem convenient of solution by applying the Work Sheet Table given in the 1939 paper on Comparative Ore Values. We determine the respective consuming-point values by running through the table the raw and the beneficiated ores, the latter being the higher in value, of course. We then ascertain the respective Lake Erie costs. The raw-ore cost will be the mine cost plus transportation cost to Lake Erie. The beneficiated-ore cost will be the mine cost and the concentrating cost both based on raw ore used, plus the transportation expense in dollars of the concentrated ore expressed in cost per ton on raw ore. Comparison of these results shows whether or not the increase in calculated value at the consuming point of the beneficiated ore pays for the ordinarily increased Lake Erie cost. We may note that in certain cases the lower freight per unit to Lake Erie may well pay the entire cost of beneficiation at the mine.

In his study of the Cleveland figures on five ores, Mr. Davis finds that in ores of equal iron content the ore with the high gangue and low moisture suffers in value as against the low gangue and high moisture. That is to be expected, as moisture does not have to be neutralized with limestone and the resultant slag smelted with coke. We believe that an

ore seller recognizes this and is willing to make a corresponding concession in regard to Lake Erie market price. After all, this price is properly to be regarded as a "basis for negotiation between seller and buyer." And quite possibly, as determined in both Mr. Davis' work and that of the writer, a concession of around 10 to 12¢ on each 1 per cent of gangue over about a 9 per cent base is not far from right under capacity operation conditions, at least.

Mr. Davis is in doubt as to what characteristic of Old Range ore accounts for the apparent willingness of the operator to pay 15¢ differential over Mesabi ore. We would answer that this is good only for a certain proportion in the burden. Some have found 10 per cent the best, some 20 per cent and some 30 per cent. The last is our experience. In screen tests we have found Old Range to be coarser in size than the unwashed Mesabi, although not so much so in the medium size separations, and not particularly coarser in any respect than the washed Mesabi, with which kind of ore we have had experience only as a minor part of the burden.

We have thought of the Old Range particle-size factor as having some effect in "opening the burden" with more voids for gas travel and intimate contact with the stock, which more than neutralized the tendency, so we supposed, of the Old Range to be somewhat less easily reducible by the gases. That the right proportion of Old Range produces less flue dust may be partly attributed to the more uniform gas travel through the voids, but we believe some of the credit must be given to the way the respective ores dry out under heat—that the Mesabi dries to a dusty condition and the Old Range dries to a somewhat plastic condition, and less of it blows over from the furnace top.

Use of Sinter in Blast-furnace Burdens

By J. H. SLATER*

(Pittsburgh Meeting, April 1940)

THERE is nothing particularly new about the use of sinter in a blast-furnace burden. For many years flue dust has been sintered at the various blast-furnace plants to put it in a form that could be recharged to the furnace with some assurance that it would stay in the second time. This paper is not a compilation of scientific data but only an attempt to give our experience with sinter. There are some unexplained discrepancies in the tests given here, such as the flue dust produced and iron tonnages, but the results given are the results that were obtained. Sinter is not the cure-all for blast-furnace problems. A good coke is still the most important factor in good furnace operation. However, *good* sinter is a big help.

As flue dust is produced under varying operating conditions and fluctuates greatly in carbon content, it is difficult to produce from flue dust alone a uniform sinter, which will give satisfactory blast-furnace results. Sinter made from flue dust alone will change in character with every carbon variation. Almost invariably flue dust contains carbon in excess of the amount necessary to make good sinter, and this excess must be burned out. This, of course, necessitates reduction of the speed of the sintering machine and thus a decrease in tonnage. An alternative is to dilute with a carbon-free material to use up the excess carbon. High-carbon material when sintered results in a very dense, undesirable product, since the excess heat melts the charge

into a hard, nonporous mass, and tends to form refractory silicates.

At the Republic Steel plant in Cleveland, there had existed since 1924 a continuous-type sintering machine having 224 sq. in. of grate-bar area, capable of producing 9 to 11 tons of sinter per hour from flue dust. Under a former management, it was the practice to sinter only the flue dust from the blast furnaces, no attempt being made to recover the gas-washer sludge. As the dust was limited, the plant operated only part time. In other words, there was a sintering plant representing considerable investment, with good facilities for screening and preparation of raw materials, and flue dust available for only part-time operation. The sinter produced was costly and not a very desirable product.

The first step was to install equipment for the recovery of the gas-washer sludge. This was done in the form of two large thickeners and a filter, which have proved very satisfactory. It was then decided to screen out the minus $\frac{3}{8}$ -in. fines from the Mesabi ores, mix them with flue dust and coke breeze when necessary, and operate the plant at full capacity.

The tonnage increased to 18 tons per hour and the product was much improved. Sintering costs fell and the product was a preferred blast-furnace material, which on an iron unit cost compared very favorably with good Mesabi ores. On the average, 40 per cent flue dust and 60 per cent fine ore was being used.

The oversize from the ore screening also became a preferred product for the

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furnaces, and, strangely enough, was generally higher in iron than the combined fine and coarse material.

Between 425 and 450 tons of sinter per day was produced, of the following material analysis: Fe, 57.80 per cent; SiO_2 , 12.10; P, 0.096; Mn, 0.98; Al_2O_3 , 2.01; CaO, 2.08; MgO, 0.20.

It happened that at this time two furnaces that were identical in every respect were operating on steelworks iron. The dimensions of the furnaces were: hearth diameter, 17 ft.; bosh, 22 ft.; bosh angle, 78° to 30 in.; stockline diameter, 16 ft.; large bell diameter, 12 ft.; height, 90 ft.; contents, 23,230 cu. ft. Both furnaces were blown with identical blowing equipment; i.e., Mesta horizontal cross-compound engines.

With these conditions it was quite natural that we should decide to see for ourselves what the effect would be of using a rather substantial percentage of sinter in a burden. For no other reason than that it was closest to the sintering plant, therefore providing a shorter haul for the transfer car, furnace A was chosen to receive all of the sinter and furnace B was to be operated on the regular ore mix.

Test No. 1

Duration, 31 days; coke analysis, 10.50 per cent ash, 1.00 per cent sulphur; wind blown, 45,000 cu. ft. per minute.

Material	Furnace A	Furnace B
Sinter used, per cent of burden.....	35	None
Iron produced, tons.....	17,360	15,681
Coke per ton iron, lb.....	1,835	2,027
Scrap per ton iron.....	None	None
Flue dust per ton iron, lb...	170	217

Furnace A showed a tonnage increase of 1679 tons of pig iron with a reduction in coke practice of 192 bbl. per ton. Furnace A made 42 lb. less flue dust per ton than furnace B, which was rather a disappointment. The flue-dust figure in each test

represents total dust; i.e., dry dust plus gas-washer sludge.

Test No. 2

For the second test it was decided to switch burdens on the same furnaces, A getting no sinter and B having approximately the same as A had in the first test. However, it was five months later before conditions were right for a comparable run. Test No. 1 was conducted in January under rather bad weather conditions, while Test No. 2 was made under ideal weather conditions.

The duration of test No. 2 was 30 days; the wind blown, 46,500 cu. ft. per minute.

Material	Furnace A	Furnace B
Sinter used, per cent of burden.....	None	36
Tons iron produced.....	15,083	18,925
Coke per ton iron, lb.....	2,050	1,730
Scrap per ton iron.....	None	None
Flue dust per ton iron, lb...	97	91

Furnace B produced 3842 tons more iron than furnace A. It drove faster and operated much more smoothly. Coke practice was better by 320 lb., and flue dust, while much lower than in test No. 1, was virtually the same for each furnace.

These results showed rather conclusively that there was a definite benefit to the furnace using sinter.

Test No. 3

It was decided to try one more experiment, dividing the 12,000 tons of sinter that was available between the two furnaces. The duration of the test was 30 days.

Material	Furnace A	Furnace B
Sinter used, per cent of burden.....	23	20
Tons iron produced.....	16,146	17,074
Coke per ton iron, lb.....	1,959	1,825
Scrap per ton iron.....	None	None
Flue dust per ton iron, lb...	112	90

Furnace B had 2100 tons of roll scale in the burden while furnace A had none, which helps to account for some of the apparent discrepancy above.

CONCLUSIONS

An advantage that undoubtedly can be attributed to the use of sinter, but which does not show in these tests, is the greater smoothness of furnace operation and consequent better uniformity of quality of the iron.

On the strength of the foregoing experience, the company rebuilt the sinter machine, so that now it has a capacity of 1000 tons per day and has to date operated at that rate for more than a year.

Various percentages of sinter have been tried, up to 75 per cent of the burden. The conclusion is that after 50 per cent there is not much advantage other than the increased iron units in the sinter, because the charge becomes so open that intimate gas-solid contact is not attained. In other words, it appears that there may be too much of a good thing.

In operating a plant of five blast fur-

naces, for instance, if sinter enough were available for 100 per cent in the burden of one furnace or 20 per cent in each of the five, the latter would be preferable. Very apparent benefits in furnace operation begin to show at 20 per cent and continue up to 50 per cent, but beyond that the benefit is doubtful.

As to the quality of sinter, it is perfectly possible to have a high-iron-bearing sinter that is an absolute detriment to a blast furnace. Our experience is that a hard, fused sinter containing large pieces is not desirable; a more fragile, porous product, most of which will pass a $\frac{3}{4}$ -in. screen by the time it reaches the large bell is the better material. Naturally, as little as possible should pass through 14 mesh; that is, what has been termed by the Bureau of Mines, "potential flue dust."

As the better ores are consumed, we shall be forced more and more toward beneficiation. At many places this has already taken place. It is necessary to crush ore in order to beneficiate, and this, of course, brings sintering into the picture. Undoubtedly the use of sinter will increase.

Production of Pig Iron in the Electric Furnace

By CHARLES HART,* MEMBER A.I.M.E.

(Pittsburgh Meeting, April 1940)

THE art of electric smelting came with the turn of the present century and owes its existence to the introduction of alternating current, which found its first wide use in the establishment of the great power plants at Niagara Falls, N. Y. Prior to that time current was largely direct. The furnaces were electrolytic in nature and found their first metallurgical use in the production of aluminum, and this process still prevails.

The normal production of pig iron up to that time was carried on in blast furnaces in which charcoal, coke and anthracite were used as the fuel. This new electric process called for sufficient carbonaceous material to reduce the oxides and impregnate the pig iron with sufficient carbon, but the remainder of the energy was to be supplied by electric power. The chemical reactions are essentially the same in electric smelting as obtains in the older blast furnace. All of these data are so well known in both methods as to need no discussion at this time, for they can be found in scientific publications and books written during the first two decades of this century.

TYPES OF FURNACES

The 40 years devoted to the practice of electric smelting may be divided into two periods of 20 years each. The first was devoted to experimentation with furnace types and with many publications on theories and processes. The second half of this term was devoted to perfecting the types of

furnaces and their active commercial operation.

The arc furnace may be found in three types: (1) the direct-heating arc furnace with the positive electrode included in the bottom and the other electrode suspended above; (2) the independent arc furnace with its electrodes entirely above the charge, which of necessity depends upon heat reflected from the roof; (3) the direct-heating series arc furnace equipped with two or more electrodes suspended from the roof.

Of these three types, only the last is used in electric smelting of iron ore at the present time. The elimination of the other types automatically removed many of the early designs, to the end that there are now only two general types in operation: (1) the "Electrometalls" or high-shaft furnace of Sweden, and (2) the low-shaft or pit-type furnace as offered by Tysland-Hole and Siemens-Halske.

The "Electrometalls" furnace takes its name from the corporation formed by the engineers that had undertaken its perfection. After trying several designs they brought forward the furnace shown in Fig. 1, which by the way is the highest development of this type of furnace as of today.¹ Note the trend in the lines, which have kept pace with modern blast-furnace design. The high-shaft furnace lends itself to skip filling and is fitted with tuyeres immediately under the crucible roof, whereby the gases are recycled and the roof preserved.

The failure of the Electrometalls furnace in Norway, because of its inability to meet

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¹ References are at the end of the paper.

silicon requirements and to use coke as the fuel, led to trials of the pit-type furnace, which is shown in an intermediate stage in Fig. 2, and which found its greatest perfection in the furnace designed by Hole¹ (Fig. 3). This type of furnace is now being

The inadequacy of the available electrodes became apparent in the early efforts at electric smelting. The early experiments with the Electrometalls furnace required electrodes with a cross-sectional area of 242 sq. in., three in number, made up of

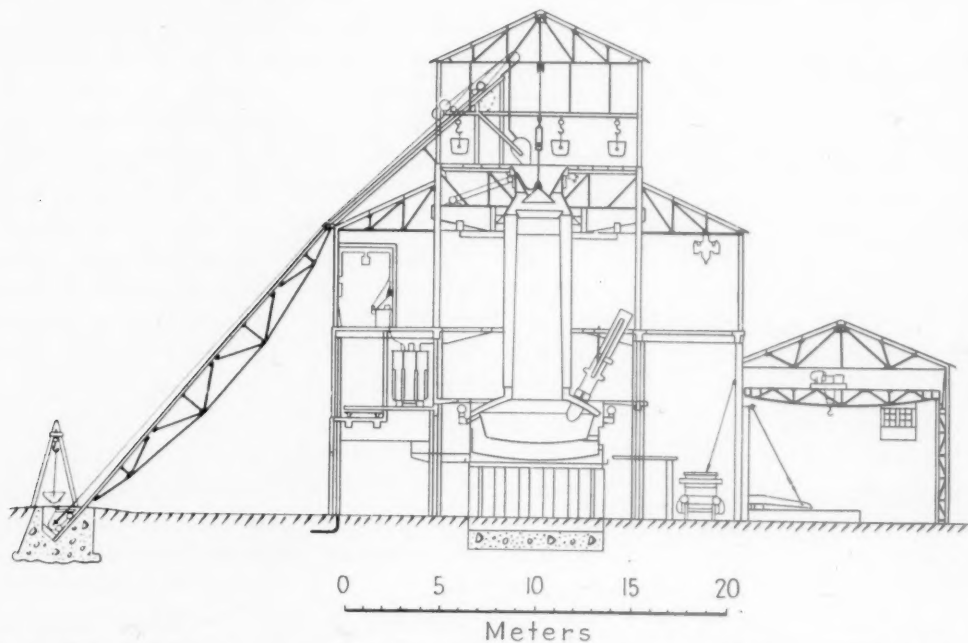


FIG. 1.—SWEDISH SHAFT FURNACE, DOMNARFVET IRON AND STEEL WORKS, DOMNARFVET, SWEDEN.¹

installed in the greatest number throughout the world. It is lateral filled, with electrodes at the angles of an equilateral triangle. The Siemens-Halske³ type (Fig. 4) is essentially the same as to electrode arrangement, but is center filled, which permits mechanical charging.

Stassano, as early as 1898, designed a smelting furnace of the independent arc type, by placing horizontal electrodes at the tuyere positions in a small furnace with lines identical with the blast furnace of that day. Its faults are apparent. Moissan tried the same principle, and also failed. Dr. P. L. T. Heroult was irrevocably committed to the direct-heating arc type. He and his disciples failed completely, and both types have disappeared from commercial operation.

smaller ones bound together, which were so short that butt-end loss was excessive and amounted to as much as 40 per cent in extreme cases. The prefabricated electrode⁴ as now produced has met all requirements, in that practically any diameter within reason is available. Excessive loss is avoided by joining the ends by screw threads, and these electrodes are essentially continuous. The Söderberg electrode² as designed consists of sheet-iron tubes welded in place and filled with electrode material as required, and in effect are continuous. The Electrometalls furnace (Fig. 1) is equipped with eight Söderberg electrodes of 28-in. diameter. The "Spigerverks" furnace (Fig. 3) has three electrodes of the same type 43 in. in diameter. This furnace and these electrodes are controlled by the

Norske Aktieselskab for Elektrokemisk Industri.²

The Electrometalls furnaces (Fig. 1), five in number, have an electric power intake of 6300 kw. each, and produce a pig iron suitable for the Thomas Gilchrist steel

heating series arc type, still with an open top. It was tried out at the Christiania Spigerverks (Oslo Nail Works) in 1925.² Ivar Hole⁵ took over in 1928 and improved upon the Tysland design by building an airtight nonexplosive furnace, essentially

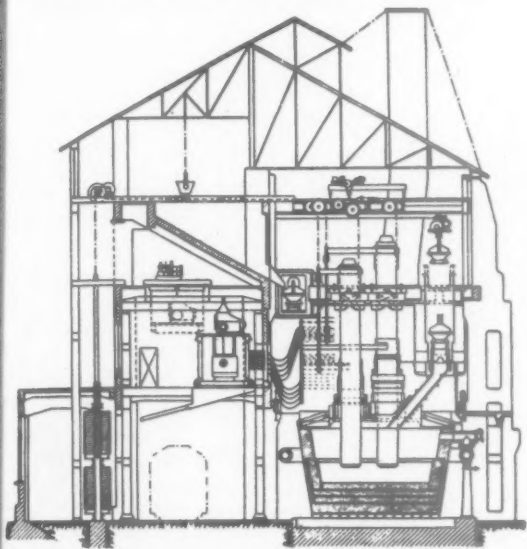


FIG. 2.—ELECTRIC LOW-SHAFT FURNACE BUILT BY SIEMENS AND HALSKE.⁶

process, using a high-phosphorus sintered magnetite. This improved furnace uses two-thirds charcoal and one-third high-ash coke and coke breeze.¹ Electrometalls electrode consumption is about 20 lb. per ton of pig iron produced, with a power consumption of 2500 kilowatt hours.²

The high-shaft furnace, although eminently successful in Sweden, failed to meet the requirements in Norway because of the lessened electrical resistance of coke when heated as compared with charcoal, and on this account failed to produce high-silicon foundry iron.

At Tinfos,² during the years 1910 to 1922, a furnace bearing that name produced pig iron with only moderate success. This furnace was of the direct-heating arc type with three suspended electrodes. It was an open-top low-shaft furnace. Tysland² brought forward the Tysland furnace in 1922, after experimentation which resulted in a direct-

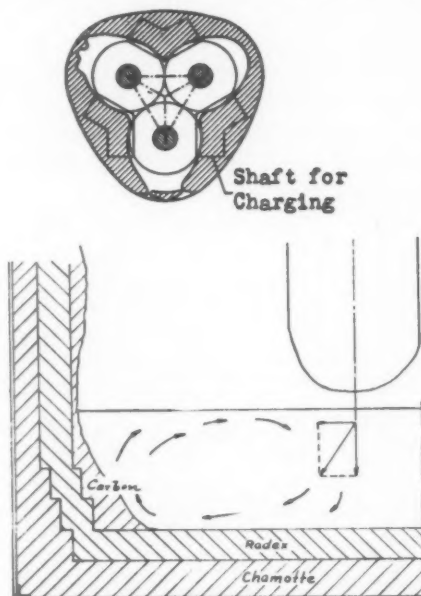


FIG. 3.—SMELTING ZONES, SPIGERVERKS FURNACE AT IMATRA WORKS,⁶ FINLAND.

From H. Willners, Supplement to Reference No. 2.

the same as shown in Fig. 4 except that it was equipped with gas-exhausting machinery.¹ Söderberg electrodes are used as indicated by the stamping room as shown.¹ The latest arrangement⁶ (Fig. 3) is trefoil in character, with electrodes placed at the angles of an equilateral triangle. Lateral charging is maintained and its advantages may be seen in the absence of erosion at the charging hoppers, as compared with that shown adjacent to each electrode—an erosion fittingly attributed to turbulence.¹¹

The Radex brick shown are made in Austria, either of magnesite or of chrome and magnesite mixed. Bricks of equal quality to this high-temperature brick are produced by the American refractory companies. The Chamotte brick are a first-grade fire-clay brick.

The location of the charging doors has a beneficial effect on electrode consumption, which is placed at 17 to 22 lb. per ton.² Owing to the use of coke, this compares most favorably with the Electrometalls practice on charcoal. The electrodes can be increased in number and as much as 175 volts may be used.² It is possible therefore to greatly increase the daily production of 100 tons now possible from a 12,000-kva. furnace. Practically all carbonaceous materials serve as fuel, but a preference for coke and coke breeze is indicated.⁶

EFFICIENCY OF FURNACES

In Table 1 relative results obtained on the two furnaces just described are shown.⁷

TABLE 1.—*Comparison of Two Furnaces*

	Electro- metalls	Spiger- verks
Charcoal per gross ton, lb.....	810	887
Electric energy per g.t., kw-hr....	2,040	2,166
Yield of ore, per cent.....	56.8	57
Agglomerates in mix, per cent....	89.1	85.5
Iron analyses, per cent: Si.....	0.50	0.62
Mn.....	1.00	0.61
Average electric load, kw.....	3,775	5,067
Average daily production, gross tons.....	44	56

The Spigerverks furnace had a rating of 9600 kw., but the highest reached was 7500 kw. It is evident that situation would have been helped materially had this furnace worked on coke, for which it is particularly designed. Therefore, all comparisons are unfair to the Norwegian furnace. The real test for these furnaces is in their commercial results. In Table 1, the Electrometalls furnace shows a material advantage over the Spigerverks in consumption of charcoal and current, and by these standards a ratio of 11 to 10 in favor of the Swedish outfit is indicated. But in reality, by figuring the costs of the materials used, the commercial ratio changes to 5 to 4 in favor of the Tysland-Hole design.

A better gauge of the efficiencies of the smelting furnaces is reflected in the analyses

of the escaping gases. Table 2 gives a comparison of the gases from the Electrometalls and Spigerverks furnaces. These furnaces worked under the most favorable conditions. The analysis of the gas from a normal blast furnace equipped with a Gayley dry blast, as reported by the late A. E. Maccoun,⁸ is also shown.

TABLE 2.—*Comparison of Gases*

Gases	Electro- metalls ²	Spiger- verks ²	Mac- coun ⁸
Carbon dioxide, per cent....	23.00	15.00	16.23
Carbon monoxide, per cent....	62.00	78.00	22.75
Hydrogen, per cent.....	1.50	1.00	0.02
Methane, per cent.....	1.50	1.00	1.39
Nitrogen, per cent.....	1.50	1.00	58.86
Ratio CO ₂ to CO.....	1:2.69	1:5.20	1:1.40
Gas per ton, cu. ft.....	18,259	22,600	132,524
Heat value per cu. ft, B.t.u....	279	292	80
Temperature of escaping gas, deg F.....	392	480	324

The CO₂:CO ratio in Table 2 is the true index of the relative efficiency of the two electric furnaces, while the Maccoun column, with reference to columns 1 and 2, indicates the relative value of the electric furnaces when compared with the blast furnace. In the former case only sufficient carbon is added to the charge to completely reduce the oxides pertinent to the operation, while in the latter the heat for fusion and other purposes is furnished by the combustion of the coke. The gases in each case respond to results obtained from the Mathesius formula,⁹ in that the Electrometalls analysis indicates some reduction above the tuyeres. The Spigerverks furnace, with neither tuyeres nor stack, indicates maximum reduction in the hearth. The Maccoun results show economy due to indirect reduction in the stack. The normal blast furnace burns seven-eighths of the charged carbon completely to CO₂, which is immediately converted into CO by the ever present incandescent coke, and at a point practically 50 ft. below the stock line the CO₂ from the flux enters the gas stream. The various reactions as between the materials in the furnace result in a gas

of the analysis shown in the third column of the table. A contributing factor to the efficiency of these three furnaces is the possibility of using the gases in auxiliary operations. Data covering this feature are shown in the table. It is impossible to con-

The great volume of gas coming from the blast furnaces, as shown in Table 2, results from the nitrogen content in the air. The blast furnace is cited as being the most efficient of all the processes used in iron and steel metallurgy. The maximum heat value

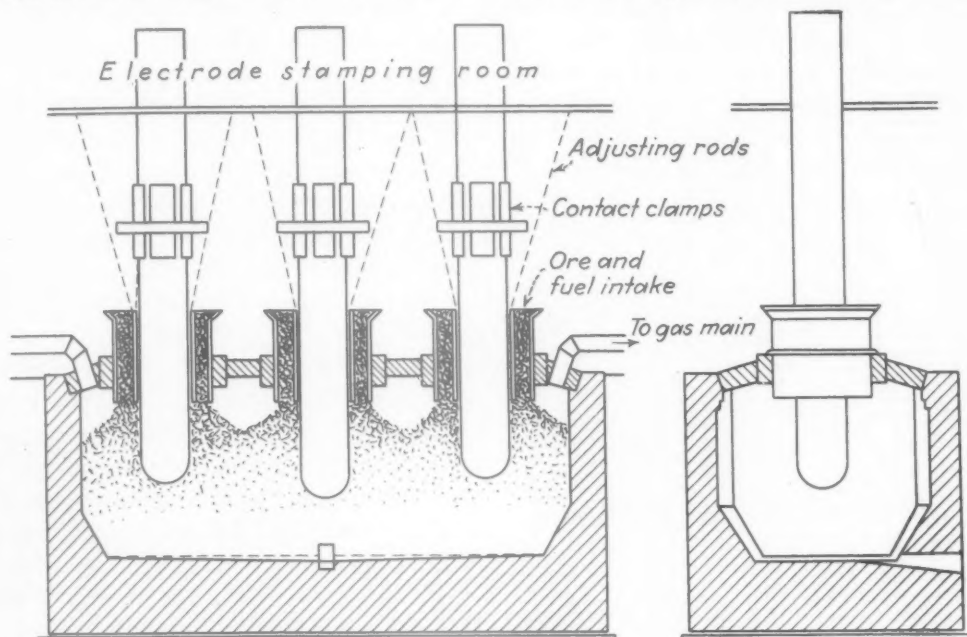


FIG. 4.—NORWEGIAN PIT-TYPE FURNACE.¹

vert the Spigerverks gas into electricity in competition with hydroelectric current, unless the cost of such power exceeds 2.33 mills per kilowatt-hour, because the current made from this gas in a modern reciprocating gas-engine plant would cost the same amount, and would be made up of 0.088 mills for operating costs with the balance chargeable to interest and depreciation. Its value as a fuel for other operations, figured at 0.9 mills per kilowatt-hour, equals approximately \$1 per ton on the pig iron produced.

The Electrometalls furnace gas shown has a lower energy value, but the reduction within the furnace was more effective owing to the recycling of the gas. Were it not for this feature, the carbon dioxide content would be 10 per cent or less and the gases would be proportionately more valuable for use as fuel.

obtainable from the case quoted⁸ is 22,000,000 B.t.u. while the calorific value of the escaping gas is nearly 11,000,000 B.t.u., of which roughly 20 per cent is available for purposes other than in the furnace operation. This, however, is increased to 70 per cent when applied to furnaces equipped with reciprocating gas engines. It would seem, therefore, that the demands upon energy is based upon the work to be done. This work varies with the types of ores used, the value of the fuels, and the quality of the pig iron desired—and there is no short cut available. Rich gases indicate poor reductive reactions in the furnace.

The carbon dioxide content in the electric furnace is of such moment that burned lime is preferable as a flux, rather than the natural stone. However, in the Swedish practice a preponderance of fines is undesirable. In Norway it has been found worth

while to use calcium ferrite, made by the Rolfsen process, as a flux.² This practice has the added feature of reducing the slag volume.

Sweden was the leader in electric smelting, and the furnaces as designed met conditions as they existed at the time the art was introduced. Norway was forced to meet existing conditions and, as already stated, turned to the pit-type furnace.

Advantages of Spigerverks Furnace

For general use and for world-wide conditions, the Spigerverks furnace has the following advantages: (1) lateral filling, which increases the life of the furnace; (2) higher voltages, which make possible increased production; (3) higher temperatures, which permit better sulphur removal; (4) use of low-grade fuels, which materially reduces costs; (5) closed type in design, absolutely explosion proof; (6) the furnace acts as a "metal mixer" as well as an "electric accumulator." These advantages give the Spigerverks furnace the call in practically all new installations, which have included two recently erected in Sweden. In spite of the great improvement manifest in these two types of electric furnaces, world production of electric pig iron is relatively small and is confined entirely to European countries. The average annual output for the years 1935 and 1936 was 205,517 gross tons, or less than 0.25 per cent of the world total for the same period.

PROMINENCE OF THIS PHASE OF IRON-MAKING

Sweden.—In the period 1935 and 1936, Sweden produced an average of 57,242 gross tons of electric pig iron, which was 9.3 per cent of that country's total output. This figure indicates a decided decline from peak operations in the year 1924, when a total of 90,000 gross tons was made, or 19.4 per cent of that year's output of pig iron. The results of operations for the year 1937

are also indicative of the trend in iron smelting in Sweden. In that year 58,810 gross tons¹⁰ of electric pig iron was produced, or 36.4 gross tons average per day for six furnaces using current in connection with charcoal. The electric current consumption was approximately 2400 kw-hr. per ton of product. These furnaces operated at an average of 243 days for the year, as compared with an average of 281 days for the 39 charcoal furnaces, which produced an average of 28.6 tons per day. The output of nonelectric iron was about evenly divided as between coke and charcoal iron, made in ordinary blast furnaces.¹⁰ The coke furnaces produced a daily average make of 130 gross tons.¹⁰

The rate for electric power in Sweden¹ was 3.5 mills per kilowatt-hour at the customers' transformers, subject to a rebate of 10 per cent to the electric smelters. In addition to this rebate, seasonal power was furnished at reduced rates, depending upon the number of months the furnaces operated during the year. These rates ranged from 0.63 mills for one month to 3.15 mills for the entire year. This schedule of rates would indicate that for 1937 the average rate paid on the 2400 kw-hr. consumed per ton of iron was 1.89 mills. In that year charcoal sold at about \$12.50 per net ton. Sweden's charcoal consumption in blast-furnace practice is placed at 1350 lb. per ton of iron, which indicates a fuel cost of \$8.44 per ton. Table 1 indicates a possible fuel cost of \$11.49 per ton on electric pig iron, assuming continuous operation throughout the year. The figures are based upon the use of agglomerated ores in the charcoal furnaces as well as in the electric furnaces.

The total annual capacity of electric smelting furnaces in Sweden may be placed at 100,000 gross tons. Sweden is credited with a total potential waterpower capable of producing 32,500,000,000 kw-hr. per year. Only 5,500,000,000 kw-hr. are now available, which represents only one-sixth

of the possible total electric energy. Viewed in this light and in conjunction with the increased costs for charcoal due to diversion of lumber products to more remunerative markets, it would seem that the electric smelting of iron ores has not been the bonanza prophesied for it at the time of the introduction of the art. Sweden, however, should be credited with being the initiator of this unique method of iron metallurgy.

*Norway.*¹⁰—Norway, for the same period, 1935 and 1936, had an average annual output of 33,497 gross tons of pig iron. Of this tonnage, 32,068 gross tons, or 92.7 per cent, was produced by the electric method with the use of low-priced and inferior coke and coke breeze. This fact emphasizes the adequacy of the pit-type furnace for Norway's requirements.

The cost of power is said to be about 1 to 1.5 mills per kilowatt-hour. This cost of power has attracted ferroalloy manufactures, to the end that 145,000 tons of these products were produced in the year 1937. In the same year 32,000 gross tons of electric pig iron was produced. The operation consumed an average of 2550 kw-hr. and 893 lb. of coke and coke breeze per ton of product.¹⁰ In addition, 4000 tons of iron was produced as a by-product in an aluminum plant operated by the Pederson process.

France.—Only meager information is obtainable as to the types of electric furnaces used in France for the production of pig iron. It is intimated that much of this iron is synthetic in nature, and the industry depends largely on scrap and ore as the materials to be smelted. For 1935 and 1936, the average annual output is placed at 53,645 gross tons, or 0.9 per cent of the country's entire production for the period. The power cost is placed at 2 mills per kilowatt-hour, and is known as "white coal."

Italy.—An interest in electric smelting in Italy may be attributed to the fact that there is a woeful lack of good coking coal, as

well as that 30 per cent of the iron-bearing materials as offered to the smelters consists of agglomerated pyritic residues. The pit-type furnace is highly appreciated because of the high temperatures obtainable, whereby it is easy to reduce the 0.50 per cent sulphur found in this material to 0.03 per cent in the pig iron. These facts account for the production of 62,567 gross tons of electric pig iron, from this material, in low-shaft furnaces. Italy produced a greater tonnage of electric pig iron than any other country engaged in this industry during the periods under discussion.

Finland.—A Spigerverks furnace (Fig. 3) of the latest design was installed at Imatra, Finland, early in 1938. It has an intake of 12,000 kva. and at a 0.90 load factor is capable of producing 30,000 tons per year. Here again agglomerated pyritic residues or "blue billy" is smelted, and the resultant iron is sold under a guarantee of 0.020 per cent phosphorus and 0.01 per cent sulphur maximum. This furnace was abundantly satisfactory and represented the last word in the Ivar Hole design. It fulfills the requirements as to being a metal mixer and electric accumulator. This is confirmed by Fig. 3, which shows the elevation of the electrode tip in reference to the furnace bottom, whereby an entire day's run of iron may be stored in the hearth, and tapped out in fractional casts. This furnace plant, if still in existence, is now under Russian domination, as Imatra is within territory ceded to that nation by a recent treaty.

General.—These comparisons indicate the conditions under which electric smelting is possible, and emphasize the favorable lineup in Norway. They also indicate relative activities in the four countries in which the art has any prominence, and the only continent on which the process has succeeded commercially.

NORTH AMERICA

In regard to smelting ore in the western hemisphere, complete failure has occurred

in every case. The causes for failure are apparent in each instance and may be attributed to improper furnace designs or to commercial troubles, which developed later.

Canada.—The fact that electric current was available in parts of Canada at rates varying between \$4.50 and \$6.00 per horsepower-year led to an interest in the art of electric smelting. A Government commission was appointed, which, under the guidance of Dr. Eugene Haanel, visited various countries in Europe where experiments were being carried on for finding the proper devices for smelting iron ores electrically. Dr. Heroult was engaged and came to Sault Ste. Marie, Ontario, in 1905. He brought with him the idea of introducing the direct-heating arc furnace, in which he had full confidence. His furnace consisted of a circular steel tank properly lined. One carbon electrode was included in the bottom and the other was suspended from above. The furnace was unenclosed. This electrode suspension led to troubles that were insurmountable and the furnace was abandoned. Haanel tried to obviate these difficulties, and a double furnace was built in which the electrode was more firmly set in place and did not contact the raw materials until they more nearly approached the hearth. Turnbull, in an attempt to embody Dr. Stansfield's "ideal" furnace ideas, then brought forward his complicated direct-heating furnace with six electrodes. This furnace also had a rotating nodulizing kiln attached. All these types were failures, although some electric pig iron was produced during the World War and 27,000 gross tons was produced as late as 1918. This operation was carried on in steelmaking furnaces by using steel scrap, and the product was a "synthetic" pig iron.

California.—In 1906 Dr. Heroult transferred to Shasta County, California, at the instance of Mr. H. H. Noble, President of the Northern California Power Co., who was trying to find new uses for electric power in addition to having an interest in

the excellent iron ore found in that county. This ore contained 68 per cent metallic iron; the sulphur was 0.021 per cent and phosphorus 0.012 per cent. Heroult still clung to the direct-heating arc principle but increased the electrodes to three in number. The closed furnace included five charging stacks, around which the escaping gases were burned. This furnace was guaranteed to make 20 tons per day. It was blown in July 4, 1907 and proved to be a failure in every way. Dr. Dorsey Lyon, after due experimentation, designed a high-shaft furnace essentially the same as the early Electrometalls furnace, of which the modern furnace (Fig. 1) is the outgrowth. The gases were not recycled but were burned in the furnace top with air introduced through tuyeres inserted just above the stock line. This furnace operated from 1909 until 1911. The next effort in California was the Noble furnace, designed by Dr. Frickey. A second and larger furnace of the same design was erected in 1913. In principle these two furnaces followed the lines shown in Fig. 4, and the fuel consisted of 60 per cent coke and 40 per cent charcoal, both of inferior quality. These three furnaces completed efforts at Heroult on the pit. All ended in commercial disaster, no doubt largely because of a rise in the power rate from \$12.50 to \$25.00 per horsepower-year.

In 1918 another pit-type furnace was built in Shasta County with an input of 1400 kw., and an effort was made to smelt the same ores previously used. Inasmuch as the costs, according to W. A. Darrah, were \$27.19 at the furnace without overhead, this attempt also ended in failure—and with it electric smelting in California ceased.

British Columbia.—The efforts in Canada and California cover the actual attempts at the commercial smelting of iron ores in North America, although Dr. Stansfield prepared a report for British Columbia that indicated a cost of \$29.75 per gross ton in

that province, with electric current delivered at \$15.00 per horsepower-year.

SOUTH AMERICA

One effort was made in Brazil, which depended upon seasonal power, a condition resulting from the use of the current by the "coffee hullers" during the summer months. This plant was well designed by K. Leander and consisted of two Electrometallurgical furnaces, each capable of producing 30 gross tons per day, in conjunction with two 6-ton converters with adequate rolling-mill capacity. An electric-steel furnace was also included, and may be looked upon as a curer of ills arising from conditions existing at the plant. This company failed in 1929—a failure attributed to the "petering" of the ore supply. This seems anomalous in a country as rich as Brazil is known to be in iron reserves, and other ores were available with a haul of less than 600 miles.

SITUATION FOR ELECTRIC SMELTING IN UNITED STATES

The foregoing data as to types of furnaces, their efficiencies, and commercial successes or failures, are essential before a conclusion can be reached as to the workability of the electric smelting furnace in the United States under present conditions. The situation now is very different from that which obtained at the time of the attempts made in California, owing to expansion of water power by the Government. It has been stated that with the completion of the Government projects, an annual output of 100,000,000,000 kw-hr. per year will be available in addition to commercial power, which as of today stands at 107,000,000,000 kw-hr. per year. These Government dams have four distinct aims—power, navigation, flood control and irrigation. These projects, except the Tennessee Valley Authority, are found west of the Mississippi River, and more particularly in the Pacific States.

Some interest in the Tennessee Valley Authority power for electric smelting of iron ore has been shown. These power plants are credited with a cost of 1.70 mills per kilowatt-hour. E. C. Eckel has made complete and excellent reports on electric smelting in the area where T.V.A. power could be used, and his reports cover not only iron, but some consideration of nickel and chromium as well. Birmingham operations would offer strong competition.

The Bonneville Dam, in the Columbia River area near Portland, Oregon, is receiving the greatest attention in reference to iron smelting. This project included navigation and its construction as a matter of course came under the control of the War Department, and physically is still in charge of that Department. The business end of the project is now under an Administrator who reports to the Department of the Interior. The Bureau of Reclamation is building the Grand Coulee Dam, which, when completed with generators installed, will provide a total capacity of 1,890,000 kw. Including the 518,400 kw. at Bonneville, the available power will thus amount to about 2,400,000 kw. now installed and under construction. The Columbia River when ultimately harnessed will have a total of 8,000,000 kw. at 10 dams, all of which have not yet been authorized. The Bonneville power is now available at \$17.50 per kilowatt-year, or 2 mills per kilowatt-hour at a 100 per cent load factor.

The smelting of iron ore with power from Bonneville Dam was investigated by the War Department, and Edwin T. Hodge¹² was employed to report on the raw materials available, and Raymond M. Miller¹ reported on the feasibility of the proposed operation. Hodge's report is most comprehensive and includes a complete résumé of iron-bearing materials throughout the world, in addition to the materials readily available to Portland. Miller's report is more pertinent to the Portland situation and much of his information will be in-

cluded in this paper. Last year Dr. Paul J. Raver¹³ made a complete summary of the information contained in the two reports mentioned, and it was published by the Department of the Interior.

This problem pertains to the Northwest, and its success depends upon the adequacy of the raw materials and their conversion into iron and steel products at a profit. Assuming that these conditions obtain, a selection of these materials and the type of furnace becomes necessary.

Ores.—Among the ores favored by Hodge and Miller may be found the Scappoose ore of Washington, at an estimated price of 7½¢, the Ship Mountain ore at 10¢, and the Cave Canyon ore at 8.30¢. Consideration is also given the El Tofo ore from Chile at 8.15¢, and possibly the Las Trucas ore from Mexico at 7¢ per unit of iron delivered at Portland. Of these possible ores, based upon cost and quality, the last mentioned would be the most desirable if conditions were stable.

Fuel.—The fuel to be considered may be either coke, coal or charcoal. The coking coals of Pierce County, Washington, offer the best source for coking operations, and are obtainable at a price whereby a coke at a cost of \$5.90 per net ton is possible, when produced in by-product ovens under the most advantageous conditions. The ash content approaches 18 per cent. Subbituminous coal suitable for electric smelting use may be had at \$3.50 or less per ton delivered at Portland, while coking coals are available at prices ranging between \$4.00 and \$5.00. Charcoal, if found desirable for the purpose, would cost \$9.00 per net ton, unless the Ruzicka methods are workable, whereby a cost of \$4.00 per net ton is assumed. Limestone of excellent fluxing quality is available at \$2.80 per gross ton.

Feasibility.—The feasibility of electric smelting depends upon the assembly of these materials at the prices indicated, and used in conjunction with power at a price

low enough to permit operation on a competitive basis. It is also evident that conversion of the materials considered above could not be done in a blast furnace on a basis competitive with iron produced on the Atlantic Seaboard or at Birmingham, plus transportation to the Pacific Coast competitive points.

Pig Iron or Finished Steel?

It would seem that this problem resolves itself into one of two alternatives, which are: (1) Should the project be restricted to the manufacture of pig iron only, or (2) should it produce pig iron for immediate conversion into steel and finished steel products?

Pig Iron.—As to pig iron, estimates have been made that indicate that with Scappoose ore and current at 1 mill per kilowatt-hour for seasonal power, No. 2 foundry iron could be produced for \$20.98 per gross ton.¹ This permits payment of 1.3 mills for firm power for a continuous operation throughout the full year. The 1-mill rate used applies to a 10-month operation. The 1.3-mills rate for a full year operation amounts to 72¢ per ton, which is sufficient to make up for the expense incurred on account of the two months idleness. It must also be considered that because of the abundance of power available at Portland any interruptions must come from the furnace operation. The idea, however, originates with the scale of rates in force in Sweden.

Costs.—Estimates of costs using El Tofo ore and electric power at the cost shown above indicate a cost of \$19.99 per gross ton of basic iron.

These costs are predicated on the use of the Spigerverks type of furnace, with Söderberg electrodes estimated at \$1.01 per ton of iron. A labor and supervision cost of \$2.66 is based upon 5 man-hours for labor alone per ton of iron, as compared with 0.5 man-hours in our modern blast-furnace practice. No credit is taken into account for

the escaping gases, in that use for them is difficult to find.

It is rumored that a company has been formed to smelt the Scappoose ore with the use of current from the Bonneville project at the going rate of 2 mills per kilowatt-hour. If the Norwegian furnace were used, the cost of foundry iron would be \$1.78 higher than the above estimated cost and would be \$22.76. It is understood, however, that a furnace that as yet has not been used commercially will be perfected and placed in operation. An experimental furnace of this type is credited with a consumption of only 1000 kw-hr. per ton. In view of the fact that a definite quantity of energy is required to convert ore to pig iron, the difference in the electric operation must be made up of carbonaceous matter, and it is apparent that the final fuel consumption must be considerably higher than in present commercial furnaces, although the escaping gases partially preheat and prereduce the ore. The type of furnace permits the use of slack coal, but it would seem that, in view of the fact that electric smelting is being considered to consume as much electric current as possible in proportion to the carbon consumed, no merit can be ascribed to a furnace that minimizes this ratio.

After a careful study of all the factors in the matter of electric smelting, Miller¹ has this to say:

Without the advantages of Bonneville power at the rates above given, the project is definitely not feasible, but with these power rates available it appears that there is some promise of a project being established on a commercially profitable basis.

Integrated Steel Plant.—The second choice, or an integrated steel plant, offers a more complex problem in that a plant to be successful must be of greater annual capacity than would be permissible in a plant producing pig iron alone. On the other hand, the steel plant with its full complement of furnaces, coke ovens, steel-produc-

ing and steel-rolling units, would offer greater economy throughout, in which all the by-products would find use within the plant itself, and costs would be materially reduced. Such a plant would be ideal, in that with the exception of the steelmaking department, where tar, coke oven and furnace gases find their best use, all other operations would consume electric energy, and as a result maximum consumption of current would be maintained. Furthermore, it is essential that the finishing departments be relatively few in number and therefore be of sufficient size to warrant low costs. It is essential as well that these departments be equipped with mills of the most modern design. It is regrettable that time and space will not permit a complete analysis of the mechanics of such an installation, the beauty of which is apparent to all steel operators.

Controlling Factors.—The commercial phase of this proposition is far more important than the mechanical make-up of the plants projected, for, after all, profits are essential to the permanency of any undertaking. Competition in raw materials and competition in the sale of the finished products are the controlling factors. In the matter of raw materials, scrap is the outstanding factor for consideration, in that it is abundant and consequently the price fluctuates with current conditions. The present competing steel companies are credited with using 90 per cent of scrap in the open-hearth mixtures, much of which is of their own making. The 10 per cent of pig iron required is produced in their own plants as well. It should be noted that the full benefit of pig iron in the mixture lies in its introduction as hot metal in sufficient quantities to reduce time of heat and fuel consumption. The disappearance of cold pig iron from the steel industry is regrettable, for even in the steel-producing centers such plants as may be without blast furnaces have been driven to the use of scrap in increasing proportions, which in

extreme cases has brought about the complete elimination of pig iron from their mixture. This trend is reflected in the amount of iron ore consumed per ton of iron and steel products produced. In the year 1890 about 2.10 tons¹⁴ of ore was required, as against an average of 0.96 tons¹⁴ for the industry as it now operates.

It is evident that the electric furnace, in order that it may compete, must produce pig iron at a much lower cost than the competitive prices for pig iron delivered at Portland. All of which leads to the conclusion that the electric energy from the Bonneville Dam will find its best uses in the production of ferroalloys and the smelting of some of the more valuable metallic ores, the lead in which has been taken by the aluminum industry, and rumors indicate a contract for 65,000 kw. for this purpose.

As to the possibilities of a steel plant, Dr. Paul J. Raver¹³ has the following to say:

It is concluded from a consideration of the problem that steel interests, adequately financed, could establish successfully a large integrated iron and steel works and a tinplate

mill in the Columbia River area, if a steady outlet for the tinplate could be assured; and further provided that the company could gain control of the most suitable and lowest cost iron ore, coking coal and limestone deposits available to the area.

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Research Problems Relating to Steelmaking Processes

Compiled by the COMMITTEE ON THE PHYSICAL CHEMISTRY OF STEELMAKING *

JOHN J. EGAN,† *Secretary*

(New York Meeting, February 1941)

THE present list of problems relating to the physical chemistry of steelmaking has been prepared by the Committee on the Physical Chemistry of Steelmaking, from answers to a questionnaire submitted to a number of metallurgists engaged in both industrial and educational work throughout the United States. The purpose of the project is to make available to research laboratories a list of problems, all reduced to their simplest terms, the solution of which would aid in creating a better understanding of the steelmaking process.

It is not intended to restrict the problems to practical steelmaking. The list also includes the study of the properties, and their correlation, as well as the physical and chemical reactions, of all substances that occur or that may be in any way associated with steelmaking operations, such as metallic substances, refractories,

nonmetallic inclusions, and the constituents of slags.

Many of the problems can be carried out in university or other research laboratories. Others may be most successfully attacked by cooperation of the research men with the operating personnel. It is the Committee's earnest wish that this cooperation be fostered.

It is requested that investigators who are working on any of the problems listed and who anticipate future publication of their results, notify the Secretary of the Committee that such investigation is in progress. Suggested additions to the present list are also requested. The Committee is undertaking to act as a clearing house for information regarding the topics in this field that are being actually studied. Interested persons are invited to correspond with the Secretary.

I. Data involved in the state of equilibrium for the various systems (laboratory work, almost entirely).

A. SPECIFIC HEATS, HEATS OF FORMATION, ENTROPIES AND FREE ENERGIES OF VARIOUS PURE ELEMENTS OR COMPOUNDS; ALSO CERTAIN TYPICAL SLAGS AND REFRACTORIES.

1. Determination of specific heats and entropies of oxides, sulphides, nitrides, etc., over a wide temperature range.
2. Determination of free energies of oxides, sulphides, nitrides, etc., over a wide temperature range.
3. Determination of the heats of formation of the oxides, sulphides, nitrides, etc.
4. Determination of the thermodynamic properties of the more important mineralogical constituents of the basic open-hearth slags such as calcium silicates, calcium phosphates, calcium ferrites, manganese silicates, FeO and Fe_2O_3 .
5. Determination of the specific heats of open-hearth slags, including liquid silicates, if possible.

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6. Determination of the thermal characteristics; i.e., specific heats, heats of fusion, heats of formation, etc., of the commonly used refractories.
 7. Determination of the heats of solution in liquid iron of the elements silicon, carbon, aluminum, etc., and the oxides, sulphides, nitrides, etc.
- B. EQUILIBRIUM CONSTANTS OR FREE ENERGIES OF VARIOUS REACTIONS.
1. Determination of the equilibrium constants of the oxidation of ferrous to ferric iron by carbon dioxide and water vapor at high temperatures and the effects of added substances.
 2. Determination, experimentally, of the deoxidizing values—i.e., equilibrium constants, (with temperature coefficients)—of all currently used or proposed deoxidizers.
 3. Study of the reaction $\text{FeO} + \text{C} = \text{Fe (Liquid)} + \text{CO}$ over a wide range of carbon content and temperature.
 4. Removal of presently existing discrepancies in the data for the equilibrium $\text{FeO} + \text{H}_2 = \text{H}_2\text{O} + \text{Fe}$ at temperatures above and below the melting point of Fe.
 5. Study the effect of temperature on the reaction, $\text{C} + \text{SiO}_2 \rightleftharpoons 2\text{CO} + \text{Si}$. Does the presence of Fe or Mn facilitate the reaction? Determination of its equilibrium constant in liquid steel. Can a carbon-free steel (below 0.01 per cent) be obtained using SiO_2 as the only source of oxygen?
 6. Study the effects of manganese, nickel, and other elements on the equilibrium $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$, or the corresponding reaction with hydrogen.
- C. EQUILIBRIA IN LIQUID-LIQUID SYSTEMS (DISTRIBUTION CONSTANTS) AND SOLID-LIQUID OR SOLID-SOLID SYSTEMS (SOLUBILITIES-PHASE DIAGRAMS).
1. Determination of solubility curves for the various carbides, nitrides, and oxides in liquid steel.
 2. Study of the formation of inclusions and their composition.
 3. Further work along the line suggested by Crafts, Egan, and Forgeng [*Trans. A.I.M.E.* (1940) **140**, 233]; i.e., What are inclusions and how do they get there?
 4. Study of aluminum sulphide inclusions [Sims and Dahle: Effect of Aluminum on the Properties of Medium Carbon Cast Steel. *Trans. Amer. Foundrymen's Assn.* (1938) **46**, 65-104].
 5. Study of the solubility of oxide and sulphide inclusions as a function of steel composition.
 6. General study of all the systems met with in steelmaking, both in liquid metal and slag; for example, Fe-FeS, Fe-FeO, Fe-S-O, Al-Al₂O₃, Mn-MnO, Mn-MnS, Mn-O-S, Mn-S-Fe.
 7. Study of the systems O-H-metal to get a clearer understanding and a more complete elimination of hydrogen in the molten alloy.
 8. General study of FeO equilibrium between slag and bath. How much of the FeO, chemically analyzed as being present, is available to enter the equilibrium, and how much may be unavailable because associated as a compound with other elements in the slag?
 9. Follow the work of Körber and Olsen on the equilibrium between metal and slag in the systems Fe-Mn-Si and FeO-MnO-SiO₂, checking and clarifying the effect of the presence of carbon in the melt.
 10. Study of the behavior, effects, etc., of nitrogen and its interrelation, if any, with carbon.
 11. Study of the distribution of FeO, S, Mn, and P between slag and metal.
 12. Determination of the effect of composition on the solubility of hydrogen and nitrogen in liquid steel.
 13. Study of the equilibrium of sulphur between slag and gas for various types of open-hearth slag.

14. Study of the use of sodium oxide in basic slags as a desulphurizing agent.
15. Study of the effect of spar addition on the ability of a slag to hold phosphorus.

D. ACTIVITIES, VAPOR PRESSURES; DISSOCIATION CONSTANTS.

1. Determination of the vapor pressure of iron as related to temperature.
2. Determination of the activities of carbon, manganese, nickel, cobalt, chromium, silicon, phosphorus, etc., dissolved in liquid iron.
3. Determination of the activity of CaO, FeO, etc., in basic slags.
4. Determination of the molecular constitution of liquid slags.
5. Determination of the form in which oxides are present in open-hearth slags; i.e., aluminates, silicates, etc.
6. a. Do the compounds in slags dissociate as in water solutions, and to what degree?
b. Are these dissociated groupings ions?

II. Other physicochemical problems, suitable for laboratory study.

A. REACTION RATES.

1. Determination of the effect of temperature and agitation on reaction rates in the open-hearth furnace.
2. Fundamental study of the mechanism of the reactions between steel and slag. In general, investigators have endeavored to determine why steel reactions run as they do, rather than to measure the rates under different conditions. One of the most important aspects of such a study would be to determine to what extent the reactions involve diffusion processes and to what extent they are surface phenomena arising from the intimate mixture of slag and metal resulting from turbulence and other causes.

B. DIFFUSION RATES.

1. Determination of the rates of diffusion from slag to metal of FeO, etc.

C. FLUIDITY AND SURFACE-TENSION DATA ON SIMPLER SYSTEMS.

1. Preparation of temperature-viscosity curves for steels of various compositions.
2. Study of the effect of dissolved or suspended oxides and sulphides on the fluidity of the bath.
3. Do oxygen and nitrogen promote the dispersion of the liquid oxide and silicate melts in liquid iron?
4. Study of changes in fluidity of steels due to the various reducing agents such as aluminum, titanium, ferrosilicon, and ferromanganese.
5. Study of the fluidity of recarburized steels as compared with the fluidity of those that have not been recarburized.
6. Study of the effect of oxidation during melting on the fluidity of steels.
7. Study of the fluidity of cast steel with special reference to the anomalous changes in fluidity taking place when the silicon content is increased from 0.10 to 0.30 and from 0.30 to 0.75 per cent.

D. MISCELLANEOUS.

1. Is there any evidence of allotropy in liquid iron?
2. Study of the mechanics of austenitic grain-size control. It has not been definitely proved that inhibition of austenitic grain growth is due to residual aluminum, aluminum oxide, aluminum nitride, or to some other combination of aluminum.
3. Study of segregation in liquid steel. This has been suggested and should be either definitely disproven or quantitatively recognized. Sulphur and phosphorus seem to be the worst offenders, but even copper is not above suspicion.
4. Study the possibility of removing residual copper from steel.

III. Problems suited to mill studies (in shops or laboratories). (Statistical methods would be prominent in most of these.)

A. REACTION RATES.

1. Study of the mechanism of the boil.
 - a. Where does the boil originate?

- b. What conditions control evolution of CO as bubbles in liquid iron?
 - c. Study of the effect of slag viscosity on CO pressure in the bath with respect to the reaction $\text{FeO} + \text{C} \rightleftharpoons \text{CO} + \text{Fe}$.
 - 2. Study of the rate and mechanism of elimination of hydrogen in the open-hearth bath.
 - 3. Study of the elimination of oxygen and sulphur in the basic electric furnace by means of calcium carbide and white slags.
 - 4. Rate of absorption of sulphur from gases by open-hearth slag.
 - 5. Study of the kinetics of the reaction in the Bessemer converter.
 - 6. Study of the speed of combustion in mixtures of air with natural gas, producer gas, by-product coke-oven gas, atomized oil, or atomized tar.
 - 7. What conditions control speed of reaction at the interface of metal and slag?
 - 8. Determination of the rate of solution of limestone in open-hearth slags.
 - 9. Study of nitrogen pickup in its relation to atmospheric conditions.
 - 10. Study of the mechanism of desulphurization in the basic open-hearth process.
- B. FURNACE OPERATION OR DESIGN.**
- 1. Study effects of working and tapping temperatures on hydrogen or nitrogen content; ingot structure; inclusion formation, and inclusion elimination.
 - 2. Study of the variations in metal composition and temperature with bath depth.
 - 3. Study relative effect of all burnt lime and all raw lime in charge with respect to: period and intensity of the boil; elimination of hydrogen; elimination of nitrogen. Is the effect the same with all hot metal as with cold metal charges?
 - 4. Study of dolomitic slags for basicity, state of oxidation, temperature-viscosity relationship, and ability to remove phosphorus and sulphur.
 - 5. Are minerals (compounds) present in the molten slag at steelmaking temperatures retained in the same proportions in rapid cooling to room temperature?
 - 6. Determination of the cause of foaming slags.
 - 7. Study of the effect of nitrogen content of scrap on the nitrogen content of basic open-hearth steel.
 - 8. Study of the relation between nitrogen and chromium content of chromium steels in electric furnaces.
 - 9. Study of absorption of gases by steel in electric furnaces.
 - 10. Study of the relation between silicon in pig iron, and the volume, chemistry, and characteristics of slag produced in basic open-hearth practice.
 - 11. Does ladle aluminum before the manganese addition have a different effect from a late addition of aluminum, on the rimming action and mold requirements?
 - 12. Does a molten addition of ferro-carbon-titanium to rimming steel in the ladle increase or decrease the mold addition needed? Is the action of titanium alone the same as that of aluminum?
 - 13. Study of the influence of pig-iron analysis on open-hearth operations.
 - 14. Study of the effect of moisture, temperature, and oxygen content of the blast on blast-furnace operations.
 - 15. Study of the ores used in the open hearth and blast furnace to determine the relative amounts of H_2O present, temperature release, etc., to develop methods of safely utilizing the high H_2O types; effects of particle size on combined moisture and temperature of release.
 - 16. Effect of deoxidation on grain growth of Fe-Cr alloys, Fe-Ni alloys, and Cr-Fe-Ni alloys from 1800°F . to the melting point.
 - 17. Study of the Bessemer process. (What are the essential differences in properties compared with open-hearth steel of similar analyses?)
 - 18. Study of nitrogen content during blow in the Bessemer process, including the effects of different compositions of pig iron and of slags, and method of blowing in the nitrogen.

19. Study of the relative efficiency of air and steam in atomizing liquid fuels.
20. Study of the relation between oxygen in steel and oxygen in slag in basic open-hearth practice.
21. Why does the time of the addition in the mold and the size of the aluminum affect the results?

C. STEEL QUALITY.

1. Study of the effect of proportions of the hot metal charge on ingot quality.
2. Study of Mn residuals and the effect on steel quality in the basic open-hearth process.
3. Study of pouring speeds and effect on steel quality in the basic open-hearth process for various grades of steel.
4. Study of the effect of increasing quantities of chromium brick and chromium mixtures in the open-hearth slag on metal quality.
5. Determination of a means of evaluating steel quality, ingot quality, and metal quality. Define these terms.
6. Effect of inclusions (type, number, size, distribution) on the static and dynamic properties of steels.
7. Effect of inclusions (type, number, size, distribution) on the machinability of steels.
8. Study of the origin of inclusions; i.e., in spouts, ladle linings, ladle and mold additions, etc.
9. Further study of the possibility of using radioactive materials, as tracers for the source of nonmetallic inclusions [see Sosman: *Bull. Amer. Ceramic Soc.* (1939) 18, 187].
10. Study of the effect of initial oxygen content and temperature on the type of deoxidation products; e.g., alumina clusters and glassy silicates.
11. Study of the effects of using two or more deoxidizers as individual alloys or as complex deoxidizers.
12. Study of the factors affecting reoxidation of metal after addition of deoxidizers.
13. Study of the freezing characteristics and their significance in various types of steel.
14. Study of the mechanism whereby sodium fluoride affects the rimming action:
 - a. Does it volatilize as NaF and help build up the gas pressure?
 - b. Does NaF merely help reduce the viscosity of the oxide film and promote the reactions $\text{FeO} + \text{C} = \text{CO} + \text{Fe}$?
 - c. Does fluorine react with Fe to form an iron fluoride, which in turn reacts with carbon to form gaseous carbon fluorides? (J. W. Mellor: *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 822. New York, 1924. Longmans Green & Co.)
 - d. Does it promote under cooling?
15. Study of the effect of gas and deoxidation products in steel on the weldability by atomic hydrogen, acetylene, and electric arc.
16. Determination of the value of intentionally added nonmetallic phases to improve the hot-working properties of difficultly forgeable alloys.
17. Study of various mold coatings as affecting surface and interior quality of various steels.
18. The derivation of a general formula to correlate chemistry to hardenability.

D. PETROGRAPHIC STUDIES ON SLAGS AND USED REFRACTORIES.

1. Study of mineralogical composition of open-hearth slags at and during various stages of the heat.
2. Study petrographically the tapping slags from a number of heats of the same grade of steel; for example, rimming heats under 0.10 per cent C. Slags will vary

in FeO and lime:silica ratio on these grades, producing varied results in deoxidation practice and steel quality.

3. Further study to settle the question of the form in which sulphur appears in metal and slag.

E. QUICK METHODS OF MEASUREMENT OR OBSERVATION (SLAG APPEARANCE, METAL FRACTURE, OR BREAKING TESTS, ETC.).

1. Development of methods for expressing and determining the basicity of open-hearth slags.
 - a. Normal slag systems.
 - b. $\text{CaO-SiO}_2\text{-FeO}$.
2. Study of the relationship among the different methods used for estimating the nature of slags taken from the open-hearth furnace, mainly:
 - a. Inspection of the slag cake.
 - b. Measurement of the viscosity by length of run.
 - c. Observation of color of powdered slag.
 - d. Microscopic examination.
 - e. Other methods.
3. Development of the viscometer for use inside the open-hearth furnace to test the viscosity of the slag at various stages of the heat. The present viscometer presents too much of the human element in sampling, and thereby gives erratic results.

F. REFRACTORIES.

1. Development of new refractory materials for pouring pits in order to prevent entrainment of fire-clay inclusions.
2. Investigation of basic material for ladle lining (dolomite brick and monolithic basic lining).
3. Investigation to determine the correct sizing of refractory materials for bottom and bank making in the open-hearth furnace in order to obtain better sintering properties at higher MgO content of the conglomerate.
4. Statistical study to determine the correlation, if any, between standard tests of refractories and performance in the open hearth.
5. Determination of the effect of extremely high forming pressures on the properties of refractories.
6. Investigation of non-spalling brick for use in steelmaking such as pyrophyllite or the incorporation of small percentages of basic slag with quartz.
7. Development of tests to determine the suitability of pouring pit refractories. (Present A.S.T.M. standard tests are not entirely suitable for this type of refractories.) The following items are suggested: resistance to spalling, load test, reheat test, slag penetration, gas permeability.

IV. Methods of measurement. (Such studies would include both laboratory and mill work, according to suitability.)

A. RAPID METHODS FOR CHEMICAL ANALYSIS.

1. Development of new and more rapid methods of determining oxygen in steels, including both the bath and solid samples; application of spectrographic methods.
2. Critical study of the rapid methods of carbon analysis, including such instruments as the carbometer, carbonalyzer, etc.
3. Development of new and rapid analytical methods for slags.

B. SPECIAL ANALYSES AND INCLUSION EXTRACTION.

1. Development of microchemical methods for identifying individual inclusions.
2. Study of the application of microradiographic methods to inclusion studies.
3. Continuation of the critical study of the currently used methods of inclusion analysis.

4. Study of the "bomb" method of oxygen determination with a view to developing information as to possible variation due to sampling, etc.; comparison with Leiber's vacuum sampling methods.
 5. Development of a method for inclusion analysis that will determine MnO in a rimmed steel.
 6. Development of a more accurate method for the determination of hydrogen in steel.
 7. Development of more accurate methods for carbon analysis (to ± 0.002 per cent in steel under 0.10 per cent carbon).
 8. Critical study of the accuracy of the spectrograph for open-hearth steel analysis.
- C. TEMPERATURE MEASUREMENTS.
1. Development of a practical method of measuring temperatures in the open-hearth furnace.
 - a. Temperature of steel bath.
 - b. Temperature of slag.
 - c. Temperature differential at metal-slag line.
 - d. Temperature at furnace bottom.
 2. Analytical study of currently used methods to determine their accuracy.
 3. Determination of emissivity of slags and molten steel.
 4. Evaluation of the effects of various elements and compounds on emissivity; for example, an appreciable difference is noted between high and low FeO contents. The higher FeO heats show higher emissivity.
 5. Study of the tungsten-molybdenum thermocouple as a possible means of measuring bath temperatures.
 6. Study of the radiating characteristics of flames of mixtures of air with natural gas, producer gas, by-product coke-oven gas, atomized oil or atomized tar.
- D. NEW METHODS OF MEASUREMENT, SUCH AS FOR VISCOSITY, SURFACE TENSION, GAS PRESSURE.
1. Development of methods for measuring surface tension of liquid slag.
 2. Development of a method for estimating or recording the intensity of the boil, especially where the rate of carbon drop is low.
 3. Study of the electrical conductivity of liquid slags and its significance.
- E. MICROSCOPIC METHODS.
1. a. Study of methods for the identification of inclusions as they exist in steel. This would include simple, duplex, and complex inclusions.
 - b. Study of the effect of various etchants, polarized light, and heat, in the identification of inclusions, as described by Scheil, Baeyertz and Vilella in the National Metals Handbook.
 2. Development of optical methods of identifying inclusions.
 3. Development of polishing technique for inclusion study.

V. Bibliographic studies and critical collection and evaluation of existing data

DISCUSSION

(John Chipman presiding)

N. A. ZIEGLER,* Chicago, Ill.—Until now problems associated with the general field known as "the physical chemistry of steel-making" have been regarded almost exclusively from the angle of manufacturing steel

ingots and their solution has been considered principally as applied to the basic open-hearth process.

I should like now to make a few remarks as a representative of a steel foundry. Mr. Egan's report gives an idea of the number and complexity of problems confronting a steelmaker, when molten steel is cast in metal-ingot molds. When the same metal has to be cased in green sand, this number increases still more. Moreover, in manufacturing pressure-tight castings,

* Research Metallurgist, Research and Development Laboratories, Crane Company.

the soundness of the metal is far more acute than in making ingots. A certain amount of porosity or "gassiness" may be allowable in an ingot: during rolling or forging it would be completely closed and welded together to such an extent that no one would ever be able to find it in the finished product. On the other hand, the same degree of "gassiness" may reject entire heats of pressure-tight castings.

I am happy to say that our laboratory is being equipped with the necessary instruments and personnel to conduct research on what we designate "physical chemistry of making steel castings" and we hope that before long we will be in a position to make our modest contributions to the science of steel manufacturing.

I should like to express a hope that the Committee on the Physical Chemistry of Steel-making will consider this problem not only from the angle of making steel ingots but also from the angle of making steel castings.

C. R. AUSTIN,* State College, Pa.—While we have not had an opportunity to survey carefully the list of topics proposed by the committee for investigation, it is clear that an excellent compilation has been effected. Our activities in post-graduate work, in the Department of Metallurgy at Penn State have been directed to studies on the properties of alloys, including reactions to heat-treatment and studies on creep. However, certain facilities are available for fundamental studies on steel-making, since we have means for preparing high-frequency induction-furnace melts and forging, rolling and swaging equipment for fabrication purposes.

Accordingly, as the program is developed and as the present warlike world efforts begin to recede, we shall be glad to assist in any way practicable.

* Professor of Metallurgy, The Pennsylvania State College.

Controlling Reactions in the Open-hearth Process

By B. M. LARSEN,* MEMBER A.I.M.E.

(New York Meeting, February 1940)

IN endeavoring to put the art of the steel-maker on a more scientific basis, as a means of securing closer control of the product, we must be severely critical of the basis of any theory we use. In particular, we must be careful to distinguish between factors that are primary and those of only secondary importance. The concentration relations that determine the slag-metal equilibria, which are usually more or less closely attained, are of course of primary significance, but a clear picture of the whole process requires that the actual rates of the several reactions be taken properly into account. At the high temperature of the steelmaking furnace, all reactions might be thought to be very rapid, but some of them in fact are not; the essential causes of this condition are important to a proper understanding of the process. This paper aims to present, and to justify, the viewpoint that the most significant reaction is the oxidation of carbon in the metal, the progress of which determines the oxygen pressure levels in slag and metal and produces stirring effects, all of which influence the course of the process as a whole.

REACTION RATES AT STEELMAKING TEMPERATURES

General experience in reaction rates makes it almost certain that at steelmaking temperatures equilibrium is attained practically instantaneously when the reactants are well distributed in a single liquid phase—that is, in the so-called homogeneous

reactions. The actual slowness of some of the reactions in the open-hearth furnace must therefore be attributed to a relatively slow rate of diffusion within the slag or metal phase, which limits the rate at which the reactants can meet each other in the liquid steel or at its surface. That the reactions can be made to go with great rapidity, by proper mixing and stirring of the reacting phases, is indicated by the following illustrations:

1. In the Bessemer process there is intimate contact between air and the whole mass of metal, and the reactions are complete in a few minutes.

2. Perrin¹ has demonstrated that by pouring liquid steel into slag contained in a deep ladle, and thereby producing almost a slag-metal emulsion, the phosphorus or oxygen content of the steel is adjusted immediately.

3. Barret, Holbrook and Wood² observed a quite rapid rate of desulphurization when powdered calcium carbide was stirred vigorously into liquid iron.

4. When a spoonful of liquid steel is poured into a mold containing aluminum wire, the formation and precipitation of alumina occurs in the fraction of a second required to freeze the surface layer of the tiny ingot. The first three examples all show that any means of increasing the effective surface between slag and metal and promoting intimate mixture of the reacting phases, thereby obviating the limitation imposed by diffusion, will enhance the speed of the steelmaking process.

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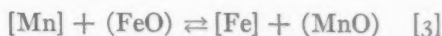
* Research Laboratory, United States Steel Corporation, Kearny, N. J.

¹ References are at the end of the paper.

To reach a clearer understanding of these kinetic relationships, it is advantageous to consider the several main reactions separately, deferring until the last the carbon oxidation reaction, which, though the most

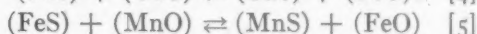
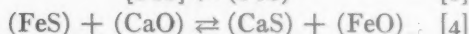
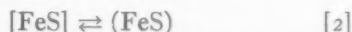
be speeded by: (1) stirring or any convection effect in either phase, and (2) any increase in area of the interface.

The manganese reaction, however, must also be written as



to describe the reaction as it occurs in the refining stage of the open-hearth process. Writing the reaction in this way implies that manganese in the metal reacts at the interface with FeO in the slag while iron similarly reacts with MnO in the slag, these reactions thus being similar to reactions 1 and 2; at equilibrium these processes balance for a fixed value of the quotient $(\text{MnO})/(\text{FeO})[\text{Mn}]$ at a given temperature. This equilibrium is substantially attained in the open-hearth furnace in a period of about an hour, as shown in Fig. 1. The change in $[\text{Mn}]$ after an addition of MnO to the slag is represented by the upper curve; after an addition of manganese to the metal, by the lower curve, which shows, moreover, that nearly 30 min. elapsed before the added manganese was distributed through the metal bath. Thus, whether manganese was added to the bath or manganese oxide to the slag, the same distribution of manganese concentration was attained for the given slag in about an hour, the total amount of manganese in each phase depending, of course, upon the relative weights of metal and slag. We conceive this limited reaction rate as a direct consequence of the limited reaction zone (the slag-metal interface) which the reactants can enter, and the products leave, only by diffusion.

The removal of sulphur from metal to slag probably proceeds by the following series of reactions.



Reactions 4 and 5 occur within the slag and probably are rapid; but bringing sulphur

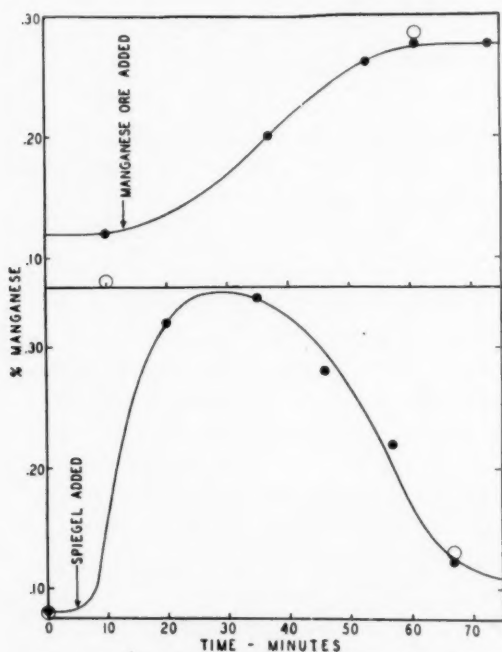


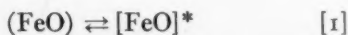
FIG. 1.—RATE OF READJUSTMENT TO EQUILIBRIUM FROM BOTH DIRECTIONS FOR MANGANESE IN OPEN-HEARTH BATH.

● Observed $[\text{Mn}]$.
○ Calculated $[\text{Mn}]$ for equilibrium with slag.

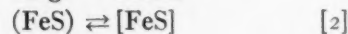
important, is the most difficult to explain satisfactorily.

MAIN SLAG-METAL REACTION PROCESSES

A simple slag-metal diffusion reaction, such as



slag metal



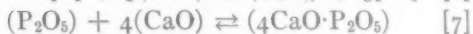
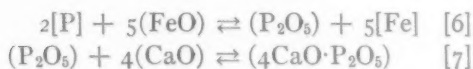
slag metal

(parentheses, as usual, denoting concentrations in slag and brackets those in metal) obviously can take place only in the zone of contact between slag and metal. It will

* In what follows $[\text{FeO}]$ is used as a convenient symbol to designate the concentration of oxygen dissolved in the metal, without implication that the oxygen is in fact present in this form.

from metal to slag involves the slag-metal interchange of reaction 2 just as in the case of manganese, and in practice we find that removal of sulphur proceeds at rates of the same order of magnitude as shown for the manganese reaction in Fig. 1 (that is, a displacement from slag-metal equilibrium for sulphur will require about the same time for readjustment).

Likewise, the removal of phosphorus presumably proceeds not by precipitation of some phosphide or phosphate in the metal but somewhat as follows:

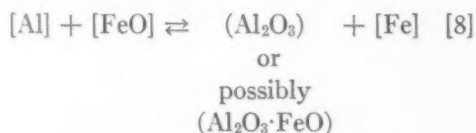


Again, although reaction 7 may attain equilibrium very rapidly, the whole process is limited by the slowness of the slag-metal interchange of reaction 6.

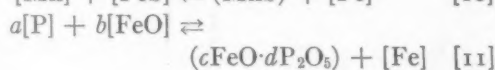
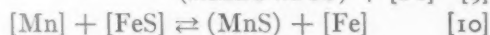
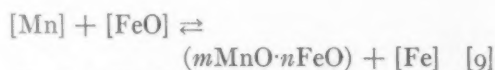
That the process of interchange of manganese, phosphorus and sulphur between slag and metal normally proceeds as rapidly as it does is doubtless due to: (1) the relatively large slag-metal interface and the relative shallowness of the bath, and, more important, (2) the formation of carbon monoxide bubbles, which stir up both layers and so quicken the transfer of the reactants to, and of the products away from, the reaction zone at the interface. Thus we already encounter here one of the many important modifying effects of the carbon reaction on the process as a whole, which are discussed in more detail later. These conditions in the furnace may be contrasted with the situation in the ladle, where there is a much smaller interface, a much deeper layer of metal, and usually no stirring by gas evolution; correspondingly the over-all rate of reaction is much smaller than in the furnace unless the factors of stirring to enhance convection and of area of interface are greatly increased intentionally, as in the Perrin process.

Reactions such as 1, 2, 3 and 6 are sometimes called heterogeneous, since they occur

only at contact surfaces between two phases, in contrast with reactions like 4, 5 and 7, which are called homogeneous because they occur entirely within a single homogeneous phase, in this case the liquid slag phase. There are also certain possible reactions (which we may seem to have dismissed without due consideration) occurring within the metal phase with the formation of a separate slag phase by precipitation from the homogeneous solution. A simple example is the extremely rapid reaction when aluminum is added to liquid iron or steel containing dissolved oxygen, which may be written:



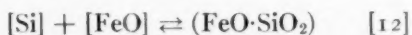
The following reactions would proceed similarly



From the point of view of reaction rate, at least, these reactions may all be considered as homogeneous, since they can occur anywhere throughout the volume of the liquid metal phase. They should all approach equilibrium with great rapidity at steel-making temperatures, but there are sufficient data to enable us to conclude that none of them can occur in normal open-hearth practice. Reaction 11 would require the presence of several per cent of phosphorus in solution. Reaction 10 often occurs in the iron mixer, but the $[Mn] \cdot [S]$ solubility product at 1500° to 1600°C. is too high to allow the reaction to occur in any normal steel bath. Reaction 9 similarly requires somewhat larger $[Mn]$ and $[FeO]$ activities than ever obtain in normal steelmaking practice.

The detailed conditions normally preventing the occurrence of reaction 9 are of some interest to the main argument of this paper. The situation may be looked upon as follows: [Mn] (in the metal) is kept low by the fact that it tends to be in balance with the (MnO) activity (in the slag), the latter being kept down by the diluting effect of lime silicates and other constituents in the basic slag. Furthermore, [FeO] is held low by the presence of carbon, which tends to form CO more rapidly as soon as [FeO] reaches a certain level in excess of the carbon equilibrium value, as will be discussed later. Here is encountered a second modifying effect of the carbon reaction on the furnace process.

Of this type of homogeneous reaction in the metal, about the only ones of any importance that probably occur in normal furnace practice are the oxidation of silicon and manganese during the melting period when, with appreciable concentrations of [Si] present, the reaction



occurs with the precipitation of silicate globules in the metal. The reaction probably is extremely rapid, being limited only by the rate of mixing and of diffusion of the reactants in solution. These silicate globules can absorb MnO, however, to form a compound silicate, so that in the precipitated slag phase MnO is present at a very low activity compared to the product of reaction 9, and thus the silicon oxidation indirectly causes the simultaneous oxidation of manganese by a rapid "homogeneous" process during the melting period of the heat.

CARBON OXIDATION REACTION

That the "inherent rate" of the carbon oxidation reaction is also very large at steel-making temperatures is indicated by the violence of the boil sometimes observed when high-carbon molten iron is added to a

bath of molten scrap with a high content of [FeO]. Yet in normal practice this reaction is usually slow, often being so slow as to remove only 0.05 to 0.10 per cent of carbon per hour. This slowness suggests that the actual rate is limited by the supply of oxygen reaching the metal through the slag, or by the circumstance that certain conditions are not favorable to the formation of bubbles of CO, or perhaps by both effects. To understand the situation more clearly, it seems necessary to try to form a more or less exact picture of the mechanism of this important reaction.

In this connection some laboratory experiments by Körber and Oelsen^{3,4} are significant. Small melts, originally carbon-free, were heated in a silica crucible under an iron-manganese silicate slag saturated with silica, the metal containing a known percentage of FeO. The crucible wall in contact with the melt usually became glazed with a slag like that over the metal, so that the latter was completely enclosed in a liquid slag envelope. When carbon was introduced into such melts, there was usually no boiling until a great excess, frequently 10 to 15 times the amount corresponding to equilibrium with the [FeO], had been added; but boiling started immediately upon the introduction of an iron wire or when the crucible wall was scratched. When the crucible was not completely glazed, boiling started after a much smaller excess of carbon had been added. These observations suggest that the initiation of CO bubbles is difficult not only within the metal phase but also at a liquid-liquid interface, whereas contact with a solid is more favorable to bubble formation, particularly perhaps if the solid is not too smooth and regular in shape.

A close parallel to this situation can be observed in many reactions that involve evolution of a gas from a liquid. A well-known example is the evolution of carbon dioxide from soda water or beer; these will hold the gas for a long time if the liquid

rests quietly in a smooth glass but the introduction of any solid that has sharp edges or is rough (for instance, sand or a swizzle stick) will immediately initiate bubbles. This will happen also even in an etched glass vessel. Just why a rough solid should initiate bubble formation is not certainly known; presumably there are tiny crevices which the liquid cannot fill because of its surface tension, so that there are in effect tiny spaces into which CO can diffuse, thus starting bubbles at those points. This is in line with the familiar fact that the most effective way of removing gas from a liquid is to pass through the latter a stream of fine bubbles of an indifferent gas; these bubbles are equivalent to a vacuum with respect to the dissolved gas, which diffuses into them and so is rapidly removed.

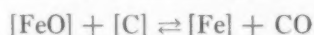
Actual observations in the open-hearth furnace are in line with the laboratory results outlined above. In the metal bath, we find only small temperature differences from top to bottom, and usually only quite small differences in carbon (or manganese) content between top and bottom; there is some evidence, however, indicating that the oxygen content tends to decrease from top to bottom, which is not surprising since the FeO must reach the metal mainly—if not entirely—by diffusion downward through the slag layer. The constancy of carbon content indicates that CO bubbles do not form readily at the slag-metal interface or within the metal; for if they did, the metal toward the bottom would be colder and higher in carbon and would, moreover, tend to be farther from equilibrium with the slag with respect to the manganese, sulphur and phosphorus reactions.

Thus we are led to the conclusion that CO bubbles do not readily start except at points of contact of the liquid metal with a solid, as illustrated by the effects of insertion of a rod or addition of scrap or ore in inducing an immediate local boil; and to the further inference that the solid surface at which the bubbles normally start is that of the bottom

or hearth where it is not coated by a glaze of slag. Bubbles so started rise through the metal, growing as they rise, and thereby cause a thorough stirring, which equalizes the composition and temperature throughout the metal layer. This interpretation of what is the initial step in the carbon reaction indicates that the rate of removal of carbon is limited by the rate of supply of either or both reactants (C and FeO) to build up and maintain a sufficient concentration in a zone close to the bottom of the metal layer and also by certain physical conditions that affect the rate of bubble formation. This inference accords with a number of practical observations, which are summarized in the following section.

VALUE OF THE PRODUCT $[\text{FeO}][\text{C}]$ IN LIQUID STEEL

The tendency of the reaction



to proceed might be considered as proportional to the excess partial pressure of CO measured by the value of the concentration product $[\text{FeO}][\text{C}]$ as compared to its value at equilibrium under the prescribed conditions. In Fig. 2, curve *A* represents the equilibrium at 1600°C. and 1 atm. CO on the basis that the constant $K = [\text{FeO}][\text{C}] = 0.01$, the concentrations being expressed in percentage by weight. Zone *B* is the range for fully 90 per cent of a large group of simultaneous tests of FeO and C taken in different furnaces when the bath is in what may be called a normal steady state; that is, in absence of unreacted ore or temporary stirring due to bottom boils, etc., and within a reasonable range of usual boiling rates. Zone *B* is considerably higher than curve *A*, which can be interpreted that in the open-hearth furnace operating normally toward the finish of a heat either there is: (1) a considerable excess of $[\text{FeO}]$ beyond that required for equilibrium with the $[\text{C}]$ then present or (2) that the CO concentration in

the liquid metal is in excess of the actual pressure. These alternatives are drawn in Fig. 3 as curves *A* and *B*, respectively,

In comparing a 0.20 per cent C steel with a 0.06 per cent C steel, both ready for pouring to make rimmed ingots, we find

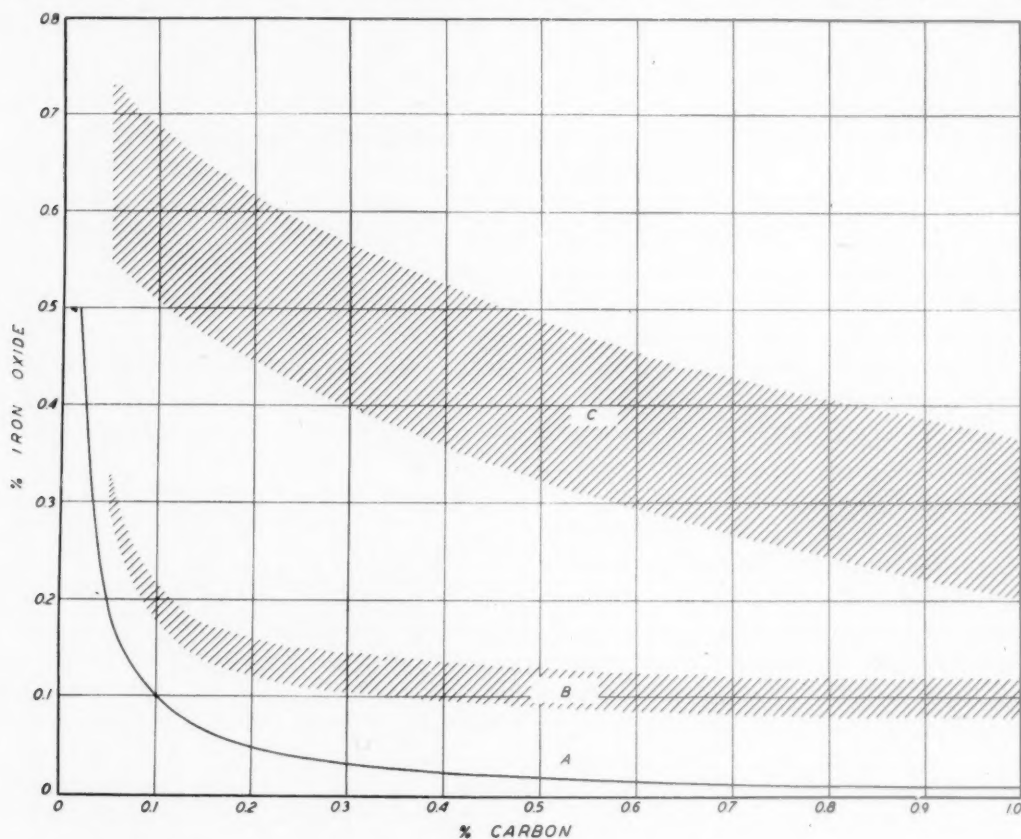


FIG. 2.

Curve *A*, C-FeO equilibrium at 1 atmosphere pressure.

Zone *B*, observed C and FeO values in steel bath.

Zone *C*, approximate [FeO] contents required for equilibrium with actual slags.

plotted from the mean values of zone *B* (Fig. 2); these represent in effect the amount of "supersaturation" of FeO and CO, respectively. There is no obvious reason why the CO pressure so derived should increase steadily with carbon content; but the indication of curve *A* that the excess [FeO] is substantially constant until the carbon content is fairly small would seem to be significant. The simplest interpretation of this constancy of excess [FeO] is that it is the "head" required to bring oxygen into the reaction zone, the rate of supply of carbon being ample until its concentration is less than about 0.10 to 0.15 per cent.

that in the former [FeO] is much smaller, but the product [FeO][C] as high or even higher, yet its rimming action—that is, its tendency to evolve CO—is much weaker. This is more easily accounted for if it is assumed that the reaction rate is largely determined by [FeO] rather than by the product [FeO][C]. Again a large group of observations on different furnaces showed little correlation between observed rate of carbon drop and values of [FeO][C]; indeed, there were cases of a rapid drop with a low value, and of a slow drop with an abnormally high value, of this product.

REMOVAL OF CARBON FROM STEEL BATH IN FINAL STAGE OF HEAT

These considerations lead to a picture of the process of removal of carbon in the open-hearth furnace that may be sketched as follows: The usual zone in which the carbon reaction proceeds toward completion by evolution of CO is not the slag-metal interface (as for the other reactions), but the surface of the bubbles, which begin to form usually only at the surface of the solid bottom or hearth. The reaction can proceed only as fast as carbon and oxygen move to these surface zones by diffusion or convection. The carbon is initially distributed throughout the metal and during all or most of any heat its molal concentration is higher than that of FeO; for these reasons, possibly also because it diffuses faster, the carbon supply is not the limiting factor in the rate, except perhaps when the carbon content is below about 0.10 per cent. The oxygen is supplied almost entirely from above, passing from the furnace gases through the slag, across the slag-metal interface and downward through the metal to the reaction zone at a rate that largely determines the over-all rate of carbon removal. The reaction itself causes stirring, which helps it along; but diffusion presumably is the dominant factor in the layer of metal immediately adjacent to the bubble surface, in accordance with the fact that some excess [FeO] seems to be required with a low rate of supply of fresh FeO to the metal even with the most vigorous stirring.

In a recent paper Styri⁵ has discussed the probable mechanism of the carbon reaction and certain rate factors in the acid open-hearth process, assuming carbon oxidation to be a rapid homogeneous reaction approaching close to equilibrium with its rate limited simply by the supply of FeO to the metal. The writer finds himself largely in agreement with much of Styri's general viewpoint on the dynamics of the process, also with the idea that the application of

conventional equations for reaction rate based upon experience with homogeneous reactions in aqueous solution, as discussed by Feild,⁶ Jette,⁷ and Schenck,⁸ is very largely meaningless when applied to this

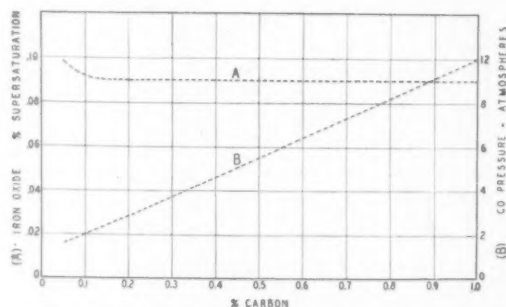


FIG. 3.—APPROXIMATE MEAN VALUES FOR (A) EXCESS [FeO] ABOVE EQUILIBRIUM, AND (B) APPARENT CO BACK PRESSURE, FOR VARYING C CONTENTS. FROM OBSERVED DATA UNDER AVERAGE BATH CONDITIONS.

reaction in liquid steel. These treatments all involve the extremely improbable assumption of a reaction proceeding within a single phase at this high temperature with such reluctance as to maintain significant quantities of the reactants present in excess of the equilibrium concentration; they have no significance as applied to any of the following three possible mechanisms:

1. The reaction might be very rapid, occurring anywhere in the metal phase wherever FeO and C are present together, and approaching an equilibrium corresponding to about 1 atm. CO pressure, as assumed by Styri,⁵ and then the rate would be dependent only on the supply rate of FeO to the metal. Besides being apparently inconsistent with various observations in practice, this assumption forces Styri to explain the observed excess of oxygen in the bath as due to "oxygen . . . inactive for reaction with carbon, most likely because it is strongly bound in silicates or aluminates which have very low dissociation pressures," an explanation in support of which there is little or no concrete evidence available.

2. The actual combination of FeO and C might occur rapidly throughout the solution to form an excess of dissolved CO, with a variable excess CO pressure due to a sluggishness in bubble formation, as discussed above. In this picture the reaction rate would be dependent on the FeO supply rate and on the physical conditions affecting bubble formation, but not on chemical concentration or activity values.

3. The reaction might be heterogeneous in character, with the actual combination of FeO and C occurring at certain boundary surfaces between gas and metal, its rate being dependent on the supply of whichever one of the reactants moves most slowly to the reaction zone, and on the area and distribution of this zone.

Mechanisms 2 and 3 appear most probable, the writer giving preference to the latter, as discussed above. There are however two other conditions, which may cause some of the very puzzling variations observed in rate of carbon drop and in [FeO]:

1. Since bubble formation apparently begins much more easily on certain kinds of solid surface, the over-all reaction rate may be affected by any appreciable variation in the area or nature of this surface; for example, by variation from heat to heat, or furnace to furnace, in the roughness or extent of slag-glazing of the furnace bottom. No very good evidence is available to the writer on this point, which apparently needs further study.

2. The carbon reaction tends to be self-stimulating (autocatalytic) because (a) it creates its own reaction zone at the surface of the CO bubbles produced, and (b) as the reaction increases in rate, the increased stirring action speeds up the rate of FeO supply by convection from the slag. In artificially stirring a bath by a cold rod or billet, or a green pole, for example, we observe a temporary drop in [FeO] followed by a quick rebound to a level usually much higher than before the stirring began. After a silicon block, a bath will usually "come

back on boil" with more violence than before the silicon addition, because of the temporarily increased available oxygen brought rapidly from the slag into the metal by the boil itself. The temporary calm and subsequent crescendo of boiling rate after a hot metal addition to a highly oxidized bath, and the frequent increasing violence of a bottom boil, are all associated with the self-stimulating character of this reaction.

CARBON REACTION AND THE OPEN-HEARTH GAS-SLAG-METAL SYSTEM

In any general picture of the operation of this process, the central fact to be kept in the foreground is the very large gradient in oxygen pressure that is always present within the melting chamber. In a fuel-fired furnace with complete combustion of the fuel over the bath, the oxygen pressure in the gas over the slag surface is on the average unlikely to be lower than about 10^{-2} atm.; this is slightly below the oxygen pressure of pure Fe_3O_4 at 1600°C ., but far above the value for pure iron saturated with oxygen or FeO (about 10^{-8} atm.), and still further above that for the average metal bath containing some carbon in solution (10^{-9} to 10^{-10} atm.). Thus there is a *ratio of oxygen pressures of around 10 to 100 million* between gas and metal, therefore a continuous flow of oxygen from furnace gases through slag to metal, and a very large departure from equilibrium in this respect; yet we have good reason to talk of a quite definite approach to equilibrium with respect to the distribution of S, Mn, P, Cr, and Si between slag and metal! The consequence is that we are almost forced to conclude that the carbon reaction is the all-important controlling factor in the over-all rate of the main reactions in the later stages of an open-hearth heat.

The fact that, in an ordinary heat, the amount of carbon removed is equivalent to 2 or 3 times the iron oxide present in the final slag, and the fact that, as also shown

by Körber and Oelsen,^{3,4} $[\text{FeO}]$ is much closer to equilibrium with $[\text{C}]$ than with the slag, coupled with this large gradient in oxygen pressure, all lead to the concept that in the slag there is an intermediate level of

oxygen withdrawal to the metal, where it is consumed by the carbon reaction. In the basic process, the slag basicity is an independent variable, and the distribution of manganese, sulphur and phosphorus is

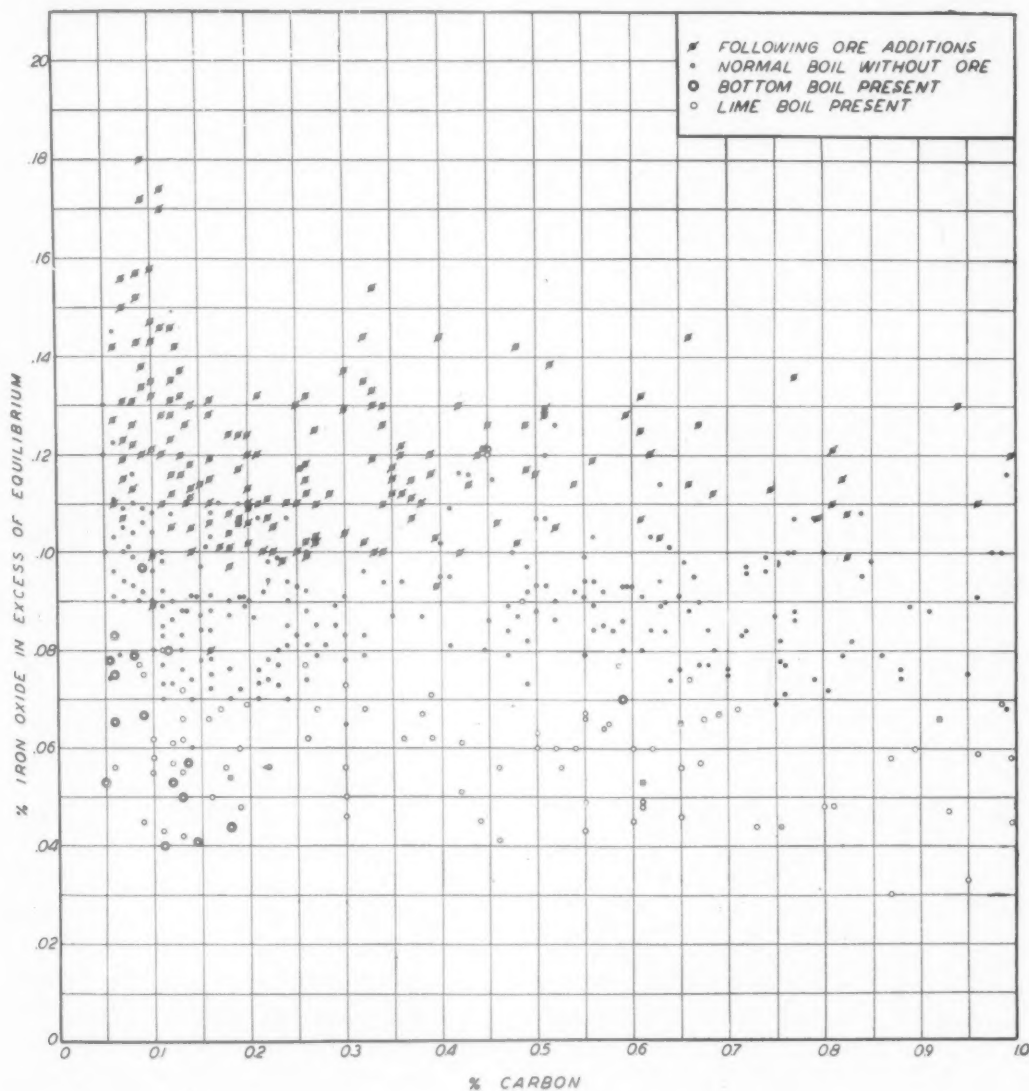


FIG. 4.

oxygen pressure,* which is the resultant of two simultaneous processes: (a) oxygen absorption from the gas phase and (b)

* The oxygen pressure (or concentration) is, of course, higher at the gas-slag interface than at the slag-metal interface, but in an active bath this difference is kept down by the mixing and reducing action of the CO bubbles.

connected only indirectly with the progress of the carbon reaction in that their distribution depends upon the oxygen pressure, or effective (FeO) , in the slag phase. In other words, that there is substantial equilibrium in these three cases is made possible only by what is in effect the stabilizing action of the

carbon reaction which, by consuming continuously the excess of oxygen reaching the metal, holds the oxygen content of the slag sufficiently constant to permit these slag-metal reactions to approach a definite equilibrium. This picture, if substantially correct, indicates that the iron oxide content of the slag, however expressed, and its relation to $[\text{FeO}]$ in the metal, will not be entirely definite or predictable by calculation, as with the distribution of manganese, sulphur and phosphorus, because it depends on certain rates of reaction and diffusion and also on other factors, such as the extent and character of the solid surface with which the metal is in contact.

The validity of this indication is confirmed by a large group of observations, made on different furnaces with a wide range of operating variables, as plotted in Fig. 4 in terms of the carbon content against $[\text{FeO}]$ in excess of the equilibrium value for that carbon content. We notice immediately a separation into fairly distinct bands, the excess $[\text{FeO}]$ being almost independent of carbon content, and (except for a slight upward trend below 0.10 per cent carbon, and a few scattered points) within the following limits for different bath conditions:

Excess $[\text{FeO}] = 0.04$ to 0.07 per cent, with a vigorous lime boil or in presence of a bottom boil.

Excess $[\text{FeO}] = 0.07$ to 0.11 per cent, in a steadily boiling bath after the disturbing effect of ore addition has ceased.

Excess $[\text{FeO}] = 0.10$ to 0.15 per cent, within a period of 35 to 60 min. after ore addition, the period varying with the character of the ore, the temperature and consequent viscosity of the slag; also within 15 to 30 min. after artificial stirring by a rod or after addition of spiegel.

It is interesting to note that $[\text{FeO}]$, though temporarily increased by an ore addition, tends to subside quickly to its

"normal" level in a steadily boiling bath; and we observe specifically that this "normal" level is not appreciably affected by wide variation in rate of carbon drop or in basicity or viscosity of the slag.

All of this points to the inference that the iron oxide content of the slag, however expressed, is not a primary factor subject to direct control, or usable directly to control the final stages of the open-hearth process, as has been implied in several published papers;* but is a secondary variable, the resultant of more fundamental factors, especially slag basicity, carbon content and temperature of the metal. Indeed, it is in a sense fortunate that this should be so because the present state of knowledge of the constitution of liquid silicate mixtures does not permit us, from the gross chemical composition of the slag, to draw any precise conclusion as to the net, or effective, concentration of iron oxide in the slag—that is, as to its oxidizing power. As a matter of fact, if we plot, for a narrow range of carbon content, the values of $[\text{FeO}]$ directly determined in the steel against the equivalent FeO or the total iron in the slag, we find that the points are so widely scattered as to furnish no indication of a correlation. If the plot covers a wide range of carbon content, however, there is a distinct correlation as shown in Fig. 5a in which the percentage of total iron is plotted against observed values of $[\text{FeO}]$; in this case the correlation coefficient is 0.71.

In Fig. 5b we have endeavored to make an approximate correction to give ordinates more closely related to the effective oxygen concentration of the slag, this correction having been carried out by the following procedure, which has been developed from a series of studies and seems to be a satisfactory first approximation. The total number of mols in 100 grams of slag was approximated by adding: (1) the equivalent number of mols $(\text{FeO})_e (= \text{FeO} + 3\text{Fe}_2\text{O}_3)$; (2) P_2O_5 as $4\text{CaO} \cdot \text{P}_2\text{O}_5$; (3) SiO_2 as

* See, for example, C. H. Herty, Jr., et al.⁹

$2\text{CaO}\cdot\text{SiO}_2$, in the more basic slags partly as $3\text{CaO}\cdot\text{SiO}_2$; (4) the remaining CaO , Al_2O_3 , MnO as such; (5) MgO to the extent of 1 or 2 per cent as such, the remainder being neglected except in the more acid slags

reaction in consuming the oxygen flowing in through the slag.

It is well known that, for a restricted carbon range, the percentage by weight of iron oxide in the slag increases with the basicity

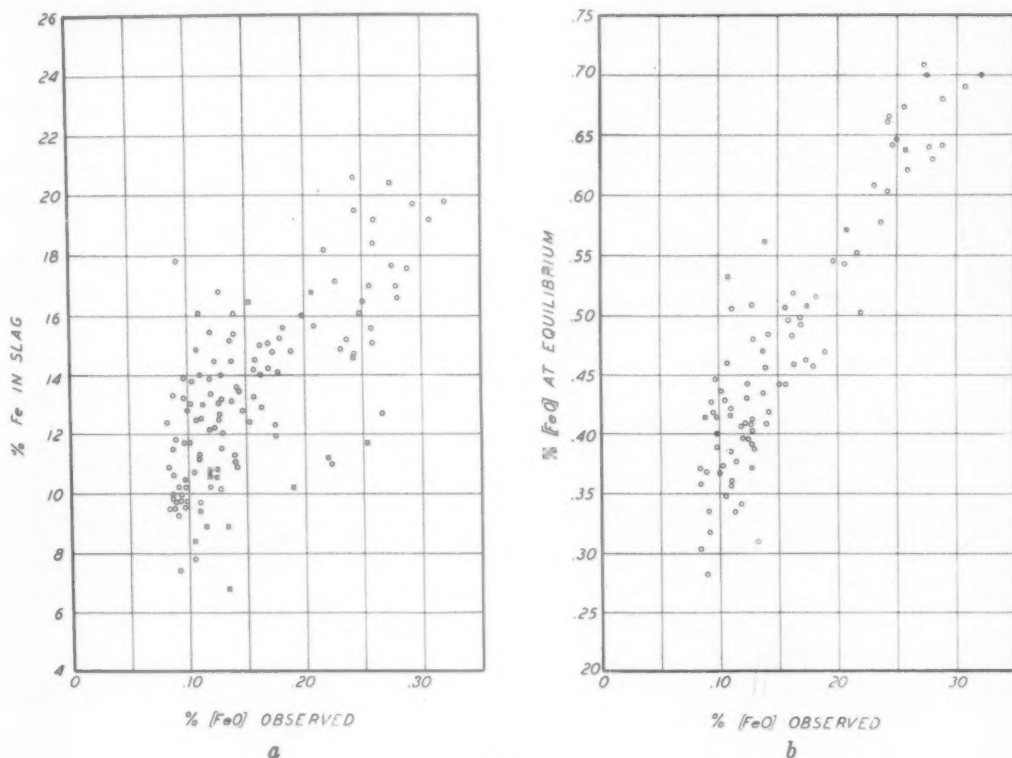


FIG. 5.

because it is present as a suspended solid phase. From this total number, the mol fraction of $(\text{FeO})_s$ is readily calculated; this fraction multiplied by the value of $[\text{FeO}]$ in equilibrium with a pure iron oxide slag at the temperature* represents the $[\text{FeO}]$ that would be present in the metal if it were in equilibrium with the actual slag. When so corrected and plotted (Fig. 5b) the correlation coefficient is increased to 0.88, indicating fairly close coupling between oxygen concentration in slag and in metal. It may be noted that the ordinates in Fig. 5b are from 2.5 to 4 times as large as the observed values, this disparity being another sign of the effect of the carbon

of the slag. Yet a plot of observed values of $[\text{FeO}]$ against slag basicity for various limited C ranges shows the points to be distributed in horizontal bands (that is, $[\text{FeO}]$ is roughly constant for varying basicity in any given $[\text{C}]$ range), which implies that with increasing basicity the percentage of iron oxides in the slag tends to increase so as to maintain for any given $[\text{C}]$ level a nearly constant *mol fraction* of FeO in the slag, again indicating how the iron oxide in slag tends to act as a secondary variable. When lime is added to the slag, the carbon reaction slows up temporarily and (FeO) increases, after which the original rate of carbon drop is reestablished. Conversely, an addition of sand lowers (FeO) and quickens the carbon reaction for

* According to solubility curve from combined data of Körber¹⁰ and C. H. Herty, Jr., et al.¹¹

a time, after which the rate of carbon drop falls to its initial value. These are again indications of the oxygen pressure in the slag being held in a "dynamic balance" with a lower range of $[\text{FeO}]$ or oxygen pressure in the metal, which in turn is held within this range by the carbon reaction. As a means of picturing this in a general way, we have plotted the theoretical $[\text{FeO}]$ values at saturation calculated as outlined above from the slag composition, against the carbon content; they lie within zone C of Fig. 2, as compared with zone B, which represents the corresponding observed values of $[\text{FeO}]$ and the equilibrium curve A.

CONCLUSION

The general "working theory" of the open-hearth bath system with the carbon reaction acting as the important fundamental control factor in the working period of the heat, as presented above, has certain logical consequences for the process control, some of which can be touched upon only very briefly here:

1. The so-called "control of iron oxide in slag" is considered to have little significance to actual operating control, as the iron oxide in the slag is a secondary rather than a primary factor.

2. The essential fundamental variables become: (a) bath temperature, (b) oreing rate, (c) charge composition and (d) slag basicity.

3. The slag basicity becomes an independent variable, which can be controlled entirely from the point of view of operating convenience and efficiency plus the attainment of requisite $[\text{S}]$ and $[\text{P}]$ contents.

4. Certain secondary variables such as slag viscosity, bath depth, speed of working, etc., tend to be reduced in importance with respect to FeO levels in the steel and therefore may be controlled, at least within certain reasonable limits, entirely from the point of view of operating convenience and economy.

Any such general picture of the mechanism of this very high-temperature process must at present involve some element of speculation; its general correctness must be judged largely by its tendency to simplify and explain various control problems. As noted at the beginning of this paper, the essential object of such theory is to develop a scientific control in simplest possible form, with distinction between the essential or fundamental, the secondary or resultant, and the inessential variables made as clear as possible.

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DISCUSSION

(J. Hunter Nead presiding)

C. E. SIMS,* Columbus, Ohio.—In this clear exposition of open-hearth reactions the author has, as usual, kept on solid ground. Little chance is left to doubt his statement that "the carbon reaction is the all-important controlling factor . . . in the later stages of an open-hearth heat." The data and arguments presented here should put an end to the il-

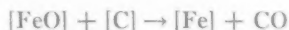
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logical but still often asserted belief that the FeO content of a steel bath can be controlled independently of the carbon content.

The statement on page 72, and curve *B* of Fig. 3, both of which indicate that the back pressure of carbon monoxide steadily increases with carbon content, suggest strongly that carbon monoxide has an appreciable solubility in steel. Furthermore, the solubility does not appear to be constant but increases with increasing *C*. The [CO], of course, would have to be in equilibrium with both [C] and [FeO], which would mean that in the absence of [C] there could be no [CO] and that increasing [C] would allow increasing concentration of [CO]. Evidence of CO solubility must be obtained indirectly because of this fact and because in analysis *C* as [C] and as [CO] are indistinguishable. Likewise, O as [CO] and [FeO] cannot be differentiated.

The postulation of some solubility is necessary, of course, for it to exert a back pressure. The question raised here is in regard to the importance and constancy of this solubility. This concept of solubility does not appear to be in conflict with the author's views on the resistance to bubble formation within a steel bath.

The assumption on page 72 that "the reaction rate is largely determined by [FeO] rather than by the product [FeO] [C]" does not seem altogether logical. Within a given system the reaction rate is determined by the concentration, that is, the opportunity for collision of the reacting substances, and the approach to equilibrium. If, as is usually assumed, CO is insoluble, the reaction between [FeO] and [C] is virtually irreversible and should be expressed thus:



Under such a condition the chance for collision, that is, the rate of reaction, would be purely a function of the product [FeO] [C].

The data presented, however, show rather clearly that the reaction rate does not follow this product, which indicates in turn that the product is not a constant for the reaction. The evidence points to the fact that CO is soluble and the reaction reversible. Thus it should be expressed as:



and the constant for the reaction is

$$K = \frac{[\text{FeO}] [\text{C}]}{[\text{CO}]}$$

wherein [CO] varies with [C] in a way that compensates for the inconstancy of [FeO] [C].

A. L. FEILD,* Baltimore, Md.—Mr. Larsen refers to my article on Rate of Carbon Elimination and Degree of Oxidation of the Metal Bath in Basic Open-hearth Practice.⁶ The article in question was the second contribution on this general subject, the first and most complete theoretical treatment having been published in the 1928 volume of the Iron and Steel Division under the same title (TRANSACTIONS A.I.M.E., vol. 80). Mr. Larsen attributes to me and to the theoretical treatment of these articles, "... the extremely improbable assumption of a reaction proceeding within a single phase at this high temperature with such reluctance as to maintain significant quantities of the reactants present in excess of the equilibrium concentration..." As a matter of fact, the theoretical treatment is equally applicable for any rate of reaction, however small or however great. If Mr. Larsen does not realize this fact, I am confident that he has failed completely to comprehend the mathematical analysis of the problem. Furthermore, it is not true that the theoretical treatment is based upon experience with homogeneous reactions in aqueous solution. The treatment is of a perfectly general nature and takes into account the heterogeneous system that prevails in the open hearth.

The equilibrium constant for the reaction between carbon and the distribution ratio between slag and metal are presumably known with a much greater degree of accuracy today than at the time these former papers were published. It would be interesting to ascertain to what conclusions our present knowledge of these constants would lead on applying them to the theoretical equations. There is no evidence that Mr. Larsen has made such an attempt. Unless the rate of reaction between carbon and FeO is instantaneous or infinitely rapid, the percentage of FeO dissolved in the metal will always be higher than the equilibrium value as long as FeO diffuses from slag to metal.

* Rustless Iron and Steel Corporation.

H. K. WORK* AND H. M. BANTA,* Pittsburgh, Pa.—Mr. Larsen is to be commended for this excellent paper and his fresh views concerning the differentiation of primary and secondary variables with respect to the control of open-hearth reactions. During recent years a majority of the investigational work has been limited to the study of FeO concentration in the slag and metal bath, with an attempt to apply certain laws of equilibrium. Mr. Larsen presents convincing arguments to the effect that this is a secondary variable, while the carbon-iron oxide reaction in the metal is the primary reaction. Recognition of the principles set forth in this paper should lead to more satisfactory open-hearth practice.

H. STYRI,† Philadelphia, Pa.—This paper was of great interest to the writer because it is the first in this country to give some support to ideas he has expressed during the past 20 years. The equilibrium conditions in the heterogeneous system slag metal should, of course, be known with some accuracy in order that the direction of a reaction may be predicted, but such equilibrium tells us nothing about the rate of a reaction in the system. As Larsen states, there should not be any doubt that the rates of reaction within each homogeneous phase of the system must be exceedingly rapid at these high temperatures and that the resulting dominant reaction in the system as a whole must be controlled by diffusion and by transfer of constituents from one phase to another. Larsen is not quite consistent, however, in designating homogeneous and heterogeneous reactions when he states that reactions 8, 9, 10, 11 and 12 may be considered homogeneous, because the end products are slags that separate from the solution when the saturation point (or "solubility product") is exceeded.

An early estimate¹² of the concentration of the constituents at equilibrium in the two phases, slag and metal, was based on the assumption of equal dissociation pressures of dissolved oxides in the steel and—it is believed for the first time—on the "free" or "active" (dissociated) oxides in the slag. It is likely that presence in the metal phase of several con-

stituents that form oxides would result in lower concentration of each constituent for a given oxygen pressure than if each constituent alone were present, and this would also apply to carbon. The reaction $C + O \rightarrow CO$ would have to be considered a heterogeneous reaction, because the end product CO separates as gas from the liquid when the saturation point is exceeded. Larsen is not correct in stating that the writer has assumed this a homogeneous reaction, although the reaction was stated to have the form of a unimolecular reaction, from which an apparent reaction coefficient K could be calculated, which would differ for various operating conditions. High values of K are indicated from such high rates of carbon elimination, which have been recorded, as 3.6 per cent in 10 min. in a Bessemer converter and 3.4 per cent in 16 min. in a high-frequency furnace. It is not likely that the oxygen in the metal phase during the carbon elimination will reach as high concentration as saturation in a carbon-free steel (say about 0.25 per cent O) even if the oxygen pressure in the atmosphere is millions of times greater than the dissociation pressure of oxygen in the steel. Only the rate of solution can be affected, and probably more by the turbulence than by the oxygen pressure.

Larsen believes that the reaction $C + O \rightarrow CO$ starts at the bottom in the open-hearth furnace, which probably is true for some conditions. It is the writer's opinion, however, that this is generally not so, but that instead the reaction takes place in the top metal layer. The following observations are offered:

1. When an acid open-hearth charge is melted down and the slag layer is very thin, the opening of a side door of the furnace may drive the slag away and a lively boil will usually start at the blank surface.

2. When later in the process boiling is dying down for some reason, which may be intentional or not, it is usually difficult to start the boiling again with either rabbling or poling or increased draft, but in an acid open hearth, at least, it is very easy to start the process again with a small lump of ore thrown on the slag near the center.

The viscosity of the slag at this point drops very quickly and the turbulence caused by the boil that has been initiated is kept alive by the blowing of the flame over the surface of the

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† Director of Research, SKF Industries.

¹² H. Styri: *Jnl. Iron and Steel Inst.* (1923).

bath and quickly spreads all over the surface. Slag drops, probably including steel drops, rise inches over the slag and fall back to penetrate the slag into the steel, where the drops come in intimate contact with the metal and provide oxygen for reaction as well as an interface where gas bubbles can form, and the boil will continue good as long as this turbulence is maintained.

If, on the other hand, the reaction $C + O \rightarrow CO$ started at the bottom, the bubbles of gas that rise would permit more gas to form on the gas interface during the ascent and quickly bring carbon and oxygen to equilibrium, and new bubbles could then not form and rise from the bottom until both carbon and oxygen in excess of the "solubility product" had again diffused to that zone.

The turbulence reached by the boil is sufficient to keep slag particles suspended in the steel, as rain will cause mud particles to be suspended in a shallow pond, and the smaller the particles the more difficult it will be to eliminate them from the steel to the slag layer above. Such suspended or emulsified slag particles are present in samples taken from the steel for analysis and the oxygen of the slag particles would be included in the total oxygen analyzed. Larsen's Fig. 4 seems to agree with this assumption that the oxygen analyzed in the samples increases with greater turbulence from the slag layer. The oxygen that is bound in emulsified slag particles is probably "essentially inactive for reaction with carbon," because it will only to a small part be "free" or "active" for combination with carbon, depending on the composition of the slag particles. The product of carbon and total oxygen found in the steel, therefore, may have no relation to the rate of carbon elimination. It would be interesting to learn what observations in practice are inconsistent with this view.

J. F. OESTERLE,* Madison, Wis.—Mr. Larsen is to be congratulated in the presentation of data of both theoretical and practical interest. While it has been many years since my contacts would have afforded me a more critical discussion, I still hold the interest that affords a keen appreciation. High-temperature

reactions are difficult to evaluate at best. To have found that diffusion is important in controlling a reaction rate is most significant.

B. M. LARSEN (author's reply).—Mr. Feild is correct, of course, in saying that the conventional reaction velocity equations are applicable to any reaction rate, large or small, and also to either homogeneous or heterogeneous reactions, *under certain conditions*. But these conditions are that no "external" factor such as a rate of diffusion, of heat flow, area of reaction zone or of catalyst surface, etc., enters in to seriously limit the reaction rate, so that the rate being measured is actually what we might call the "true" or "inherent" reaction rate. The latter is based on the idea that a mixture of molecules, usually in a gas or liquid phase, contains some that can react with each other, but in order that reaction may occur the molecules involved must (1) have a certain minimum energy level and (2) be in certain points in space relative to each other. The reaction rate is then dependent mainly on: (1) the temperature, which determines the proportions of each kind of molecule that has the minimum energy required for reaction, and (2) on certain concentrations or activities of the various molecules that determine how often the spatial arrangements needed for reaction will occur. But the conditions required for measuring this so-called inherent reaction rate are obtainable in relatively few practical cases, and almost never in high-temperature reactions.

This is because in most cases the molecules must (1) be moved into certain positions or conditions of "mixed-upness" then (2) react together, and (3) the products of reaction must in many cases move away again in some manner, for the reaction to continue. This generally constitutes some sort of chain of events, the over-all rate of which will be the resultant of several individual rates of one kind or another. Very often one of these links in the chain will be very much slower than the rest; then the rate of this slowest process and the over-all or observed rate of reaction will be nearly equal.

This important practical point is so seldom emphasized in the literature that we may perhaps be pardoned for dwelling on it a bit in this discussion. Take the reaction at room

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temperature between solutions of NaCl and AgNO₃ to form a precipitate of AgCl, which we might observe by measuring the rate of change in opacity of the liquid mixture. Under ordinary conditions of mixing, the reaction will almost certainly progress more rapidly than the convection plus diffusion process involved in the mixing, so that we should be measuring the rate of this process rather than a rate of reaction. If we could increase the mixing rate almost without limit, we should find the precipitation occurring faster and faster, but assuming sufficiently rapid measuring technique, we would ultimately approach a maximum rate, which would probably then be the true reaction rate.

Or suppose that we have a group of 1-in. spheres of Fe₂O₃ at 900°C., and we measure their rate of reduction to metallic iron in a rapidly flowing stream of carbon monoxide. After the first surface layer of iron is formed, (1) the CO must diffuse in to the oxide, (2) CO molecules are adsorbed on FeO crystal surfaces and evaporate again in part as CO₂ molecules, and (3) the excess of CO₂ must diffuse out again to maintain CO/CO₂ ratios above the equilibrium. Reduction-rate values here will be resultants of this chain of processes, probably limited mostly by the rate of step 3. Higher temperatures will increase the rates observed but not as rapidly as would be expected from conventional reaction-rate equations, because the observed increase will be largely conditioned by the smaller effect of higher temperatures on diffusion rates. Subdivision of the lumps will increase the rate but even at the highest practical values of fineness of lumps and rate of gas flow we should be still observing a rising reduction rate at constant temperature; in other words, we should not be able to approach the rate of step 2, the inherent reaction rate, in any practicable setup.

Coming now to the carbon oxidation at still higher temperatures, we would expect, *a priori*, that the "inherent" rate of reaction would be too high to measure. We do find an excess of $[\text{FeO}] \times [\text{C}]$ above the equilibrium values, however, so we say, well, perhaps this is a peculiar case of a "true reaction rate" at observable speeds at such high temperatures. But examining further, we find that under certain conditions of violent mixing and oxygen supply, as

in the Bessemer converter, the reaction rate can increase with no observable limit, and when we attempt to correlate the excess of reagents with rates of carbon oxidation in the open-hearth refining period we find little or no relationship. (Three separate groups of data with $[\text{FeO}] \times [\text{C}]$ plotted against rate of carbon drop gave nearly perfect "shot-gun patterns" with only a slight trend in the expected direction, so these were not included in the paper.) But this merely brings us toward the conclusion that had the greatest *a priori* probability anyhow; i.e., that measured rates of this reaction are not true or inherent reaction velocities, but are the resultants of many factors of which the rate of supply of FeO is apparently predominant in many cases. Then, in addition, we observe such peculiarities as that of a spoonful of steel with 2 to 3 times the equilibrium $[\text{C}] \times [\text{FeO}]$ product lying perfectly quiet sometimes in a well-slugged container and then suddenly breaking into a rather vigorous boil as the metal starts to freeze. We also remember the observations of Körber and Oelsen² of metal containing as much as 10 times the equilibrium product of the reagents with no reaction and then a sudden violent boil upon stirring with a metal wire or scratching the crucible walls; also, certain cases of inexplicable sluggishness in the open-hearth bath; and it becomes pretty obvious that we are dealing with a more or less complex set of effects which we should not even expect to be able to squeeze into the straight jacket of simple theoretical reaction velocity equations.

The suggested mechanism for the carbon reaction in this paper as a heterogeneous reaction occurring only at gas-metal interface surfaces should not be interpreted as an attempt to give the last word on this subject, and in this connection the suggestions of Mr. Sims and Dr. Styri are very welcome. The suggestion by Mr. Sims of a CO solubility that increases with carbon content would suggest a variant of mechanism 2 in the paper. If coupled with the assumption of a variable effective CO back pressure depending upon certain physical factors of stirring, roughness of solid container surfaces, etc., this would offer a possible explanation for most of the observed effects. There are apparent objections, however. For one thing, the literature on gases in metals gives in general no indication that

such compound gas molecules as CO can exist as such in either solid or liquid metal solutions. For example, hydrogen dissolved in a number of liquid metals, including iron, appears to be completely dissociated into atomic units. Also, an apparent increase of five times in CO solubility between 0.1 and 1.0 per cent carbon (Fig. 3) is a little difficult for the writer to accept. Whereas if we postulate a heterogeneous reaction at surface zones, the CO may be nearly or completely dissociated into oxygen and carbon atoms, and since these must then diffuse to the surface zones of reaction, it is much easier to accept the presence of an excess of one or both reagents.

It is true that in these surface zones the reaction rate will depend on the $[\text{FeO}] \times [\text{C}]$ concentration (plus the effective area of such surfaces) and if the true rate of reaction is very large the concentrations will be close to equilibrium in such zones, but the average concentrations observed in the mass of liquid (which is what we get by analysis) may be considerably above equilibrium because of the necessity for concentration gradients to supply FeO and C to the supposed heterogeneous reaction-zone surfaces. The assumption that CO is virtually insoluble does not mean that the reaction must be irreversible. If, depending on the C and FeO concentrations, CO and CO_2 molecules are formed at, and evaporate with a certain rate from, metal surfaces into the gas phase, it follows that CO and CO_2 can also be adsorbed on these surfaces and dissociated into C and FeO units as they pass into solution, at certain other rates depending on the CO and CO_2 pressures, and the equilibrium is the balance between these opposing rates just as much as though the process were a balance between opposing rates of evolution and absorption of a dissolved gas.

Dr. Styri's suggestion of emulsified slag droplets as explaining the observed excess $[\text{FeO}]$ values must be considered as a possibility, even though it seems an unlikely one. In the sampling of liquid steel for FeO analyses, the metal enters a heavy-walled mold containing fine aluminum wire and freezes very rapidly.

In the analysis the oxygen reported is only the portion that reacts with the aluminum to form fine Al_2O_3 particles in this very short time period before freezing; the dissolved FeO would probably react very rapidly but suspended particles of a separate slag phase should react relatively slowly; this is not certain, however. Of course, various observed effects such as those of Körber and Oelsen,³ the lower $[\text{FeO}]$ levels during bottom boils or lime boils, etc., are not very well explained by this assumption of emulsified slag. In the writer's opinion, the degree of agitation in the open-hearth bath is hardly sufficient to do much intimate intermixing of slag and metal, with the specific gravity ratio of around 1:2.

Dr. Styri's observation of lively boiling in an area of metal exposed to the gas phase is quite understandable. Under the mechanism suggested in this paper, the carbon oxidation could easily occur at the metal-gas interface where metal is exposed directly to any gas phase; also, absorption of oxygen will be speeded up in such areas if air sweeps over the surface and the extra dissolved FeO will diffuse downward to stimulate a deep-seated boil. That some of the boiling around ore lumps starts in upper layers of metal, probably right on the lump surfaces, seems quite probable, but in general the evidence suggests that these bubbles start normally at deep layers in the bath and mainly on the bottom surface; in fact, in the writer's opinion *it is the presence of such a deep-seated bubble formation that makes the open-hearth process a commercially practicable one*, because of its effect on heat flow and the speeding up of refining reactions.

Dr. Styri's criticism of the writer's consideration of certain precipitation processes as homogeneous reactions may be justifiable since the *equilibria* are heterogeneous in character. On the other hand, if it is assumed that these reactions can occur throughout the whole volume of a liquid phase, and the relief of supersaturation of the product can occur easily by precipitation anywhere in this volume, then from the point of view of *reaction mechanism and rate* it seems more logical to call the reactions homogeneous.

Effect of Temperature and Basicity upon Equilibria of Liquid Steel and Basic Oxidizing Slags

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(New York Meeting, February 1941)

IN the study of the chemical reactions occurring in the open-hearth furnace, it is frequently assumed that a condition of equilibrium between slag and metal is attained. In order to test this assumption it is necessary to have dependable operating data as well as an exact knowledge of the equilibrium state.

Considerable progress has already been made in the study of slag-metal equilibria, notably in the earlier work of Herty¹ and of Oberhoffer and Schenck² and in the more recent researches of Krings and Schackmann³ and of Koerber and Oelsen.⁴ None of these investigators, however, have employed basic slags comparable to those encountered in basic open-hearth practice, so that up to the present time our only information regarding the equilibria of these slags is based upon observations drawn from steelmaking practice in which there is little assurance that actual equilibrium was attained.

The original plan of this investigation was to secure simultaneous slag and metal samples at intervals during the making of an open-hearth heat, recording the heat history in detail and obtaining complete analyses of slag and metal, then to bring these slag samples into equilibrium with

liquid iron in the laboratory induction furnace and thus to determine directly whether or not the observed relationships in the open hearth represent conditions approaching equilibrium. This plan was only partly successful. While slags were obtained from the open hearth under satisfactorily recorded conditions and these were remelted in the laboratory under equilibrium conditions, changes in slag composition, which accompanied the remelting operation, were so great that the final slag from the induction furnace bore little resemblance to its open-hearth parent and the direct comparison was therefore abandoned. The results, however, lie within a range of slag composition that is of interest in the making of low-carbon steel. As far as we are aware, they represent the first published laboratory study of equilibria involving slags that contain all the constituents of basic open-hearth slag.

EXPERIMENTAL HEATS

The first set of measurements on slag-metal equilibrium was made in the Research Laboratories of the American Rolling Mill Co. at Middletown, Ohio. This will be known as series A. The second set was made in the Metallurgical Research Laboratories at Massachusetts Institute of Technology, and will be referred to as series B.

Series A.—The induction furnace used has been described.⁵ Approximately 1 kg. of a special ingot iron containing less than

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¹ References are at the end of the paper.

0.008 per cent carbon and 250 to 350 grams of open-hearth slag were used in each heat of series A. Normally all the metal and from 150 to 250 grams of slag was recovered in the copper mold. Occasionally, owing mainly to trapping behind an undercut edge of the crucible but partly to excessive penetration of the magnesium oxide crucible, the slag recovered would amount to only 50 grams. The time elapsing from the point when the slag temperature reached 1540°C. (2800°F.) to pouring varied between 45 and 75 min., the average being about one hour. In general, the ingots were free from blowholes and entrapped slag. Great care was exercised to secure representative samples for the metal analyses.

The doubt arising as to the accuracy of the temperature measurements⁵ was the reason for performing the series B experiments.

Series B.—The large induction furnace and the general methods of running a heat in the apparatus at Massachusetts Institute of Technology are described elsewhere.⁶ In this case an ingot-iron charge weighing 30 kg. was first melted in vacuo to reduce the carbon content to about 0.005 per cent. The furnace was then opened and 1300 grams of basic open-hearth slag and 230 grams Fe_2O_3 were placed on top of the metal. The cover and graphite heater block were replaced and a slow stream of nitrogen was passed into the furnace. After time had been allowed for equilibrium to be reached, the temperature was measured and metal and slag samples were withdrawn from the furnace. Additions of slag, Fe_2O_3 or SiO_2 as required were made or the temperature changed, and after 35 to 60 min. under the new conditions the temperature was again measured and samples were taken. These operations were repeated until 12 sets of conditions had been obtained, representing roughly three temperature levels and three lime-silica ratios.

Temperature measurements in these runs were made with W-Mo thermocouples pro-

ected by thin silica tubing. The thermocouple wire had been carefully calibrated up to 1750°C. against Pt, Pt-Rh couples. In spite of the use of a graphite heater with a heavy molybdenum insert, there was evidence in these heats, as well as in series A, that the top of the slag was at a lower temperature than the metal. The consistency of the results, however, supports the assumption that thermal equilibrium existed between the metal and the bulk of the slag layer and that chemical equilibrium was attained between metal and slag in virtually all heats. The thermocouple measurements were taken in the liquid metal and are considered reliable to $\pm 10^\circ\text{C}$.

EXPERIMENTAL RESULTS

The slag and metal analyses are summarized in Tables 1 and 2. Some metal samples gave indications of oxygen segregation. For these cases a large number of oxygen determinations were made and the average was taken; a considerable fraction of original ingot was used in the analyses. For convenience in making the many computations required in this study, the slag compositions were converted to mol fraction. While all the slags contained small amounts of chromium, titanium and other elements as well as somewhat larger amounts of aluminum, these elements were neglected in computing the mol fractions. Check calculations for cases where the more complete analyses were available showed that no important change occurred when the mol fractions were taken on the basis that CaO , MgO , FeO , Fe_2O_3 , SiO_2 , MnO , P_2O_5 and S totaled 100 per cent.

DISCUSSION OF RESULTS

The available results include not only a wide range of slag and metal compositions but also a considerable range of known temperatures. This made it incorrect to treat the various "equilibrium" relations as functions of slag composition alone. In this investigation, therefore, all the treat-

ments were based on the van't Hoff equation, one form of which is

$$d \log K = \frac{-\Delta H}{4.575} d \left(\frac{1}{T} \right)$$

where K is an equilibrium constant, T is

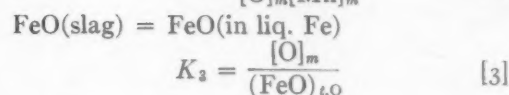
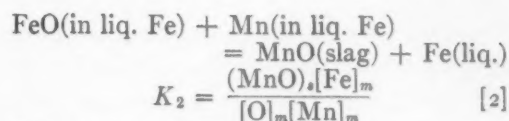


TABLE 1.—Data for Series A

Heat No.	Temperature, Deg. C. ^a	Slag Analyses, Per Cent								Metal Analyses, Per Cent	
		SiO ₂	CaO	MgO	FeO	Fe ₂ O ₃	MnO	P ₂ O ₅	S	O	Mn
8	1736	11.11	27.49	9.78	40.70	4.87	3.30	1.90	0.07	0.183	0.038
9	1791	10.11	33.90	9.42	33.10	5.69	3.70	2.06	0.12	0.142	0.076
10	1757	10.38	36.93	8.43	28.27	7.23	3.89	2.23	0.13	0.119	0.079
11	1807	9.60	34.62	9.54	32.80	4.33	4.07	2.10	0.12	0.138	0.094
13	1679	14.18	45.51	7.24	16.36	3.14	4.78	2.95	0.16	0.050	0.143
15	1766	12.89	42.90	7.85	22.95	3.16	4.61	2.70	0.15	0.085	0.134
16	1810	11.98	43.50	8.44	22.00	3.55	4.58	2.75	0.17	0.101	0.144
17 ^b	1721	13.36	45.45	6.62	18.80	3.47	4.86	3.23	0.18	0.067	0.139
18	1769	17.70	45.90	7.35	14.12	1.98	5.52	4.10	0.13	0.075	0.184
19	1780	15.77	45.70	7.85	16.21	2.45	5.53	3.72	0.16	0.079	0.183
20 ^c	1764	11.20	41.44	8.48	24.60	3.77	4.79	2.60	0.15	0.099	0.119

^a Calculated from equation 7.

^b Cr₂O₃, 0.25; TiO₂, 0.38; Al₂O₃, 2.26 per cent.

^c Cr₂O₃, 0.27; TiO₂, 0.31; Al₂O₃, 1.57 per cent.

absolute temperature and $-\Delta H$ is the heat liberated by the reaction. If ΔH is assumed to be constant—and, indeed, the data permit little else—the plot of $\log K$ against $1/T$ should be a straight line.

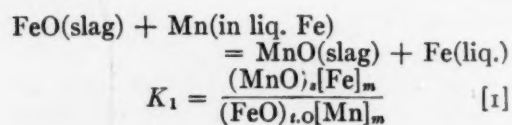
In the calculations of the equilibrium constants which follow we have used the weight per cent of oxygen in the metal instead of the mol fraction of FeO in the metal; this has been justified by M. G.

TABLE 2.—Data for Series B

Sample No.	Temperature, Deg. C. ^a	Slag Analyses, Per Cent								Metal Analyses, Per Cent	
		SiO ₂	CaO	MgO	FeO	Fe ₂ O ₃	MnO	P ₂ O ₅	S	O	Mn
2	>1620	4.76	13.34	5.71	65.03	6.81	2.18	0.69	0.06	0.196	0.0117
4	1602	5.52	16.10	5.34	61.00	7.10	2.47	0.85	0.08	0.193	0.0138
7	1592	5.73	16.78	4.71	60.16	7.63	2.39	0.90	0.09	0.170	0.0130
9	1559	5.96	16.88	4.76	60.04	7.62	2.34	0.88	0.09	0.160	0.0103
11	1684	6.44	19.03	6.58	56.00	6.65	2.85	0.87	0.08	0.212	0.0204
13	1695	8.07	18.31	7.44	55.49	5.73	2.86	0.85	0.10	0.234	0.0224
15	1642	8.77	18.64	7.10	53.73	6.24	2.90	0.83	0.08	0.207	0.0180
17	1602	9.49	18.97	6.35	53.22	6.38	2.83	0.90	0.08	0.175	0.0138
19	1567	9.57	19.11	7.95	53.08	6.73	2.76	0.95	0.10	0.157	0.0126
21	1570	15.57	22.46	5.42	43.68	5.73	3.36	1.15	0.11	0.100	0.0126
23	1643	14.74	20.80	6.98	45.44	5.76	3.19	0.98	0.08	0.214	0.0193
25	1707	12.91	19.34	8.32	47.97	5.56	3.18	0.79	0.09	0.232	0.0236

^a Thermocouple.

Data are available for the following reactions:



Fontana and J. Chipman (ref. 7). We have also used the weight per cent of Mn in the metal. The quantity $[\text{Fe}]$ is set equal to unity. For the slag composition, however, we have used mol fraction. For the ferrous oxide content of the slag we have used the

total FeO defined by

$$(\text{FeO})_{\text{t.o}} = (\text{FeO})_{\text{s}} + 3(\text{Fe}_2\text{O}_3)_{\text{s}} \quad [4]$$

where the symbol ()_s refers to analyzed mol fraction of the slag. By means of this equation, the total oxygen combined with the iron in the slag as oxides is calculated to FeO.

Because accurate temperature data were secured in the series B experiments, we shall begin with them. Reaction 1 represents the manganese equilibrium relation in its more common form. When $\log K_1$ was plotted against $1/T$, the 12 points fell on three sensibly parallel but widely spaced lines. It was evident immediately that the top line represented the slags high in SiO_2 , the middle line intermediate SiO_2 and the bottom line low SiO_2 . The constant K_1 was multiplied by a number of factors depending upon slag compositions in the attempt to get all the points on a single line. Included was a "base to acid" ratio, expressed in mol fractions, representing the lime-silica ratio corrected for phosphorus as follows:

$$R = \frac{B}{A} = \frac{(\text{CaO})_{\text{s}}}{2(\text{SiO}_2)_{\text{s}} + 3(\text{P}_2\text{O}_5)_{\text{s}}} \quad [5]$$

It was then noted that of the three lines mentioned above the upper represented slags with $R < 1$, the middle R from 1 to 1.3 and the bottom $R > 1.3$. These plots are shown in Fig. 1. Point 21, series B was given little consideration on this figure. With any of the functions of K_1 tried, it was far off the line. When $\log (K_1 \cdot R)$ was plotted against $1/T$, three lines were again obtained but the order was reversed and the position of the middle line somewhat uncertain.

When, however, the square root of this base-acid ratio was used, virtually all the points fell reasonably well on a single straight line, as shown in Fig. 2, where $\log (K_1 \sqrt{R})$ is plotted against $1/T$.

Plots for the oxygen-distribution coefficient K_3 (Eq. 3) showed exactly the same

type of behavior. With $\log K_3$ vs. $1/T$ three straight lines were obtained, the uppermost corresponding to high SiO_2 and $R < 1$. With $\log (K_3 \cdot R)$ vs. $1/T$, three lines with

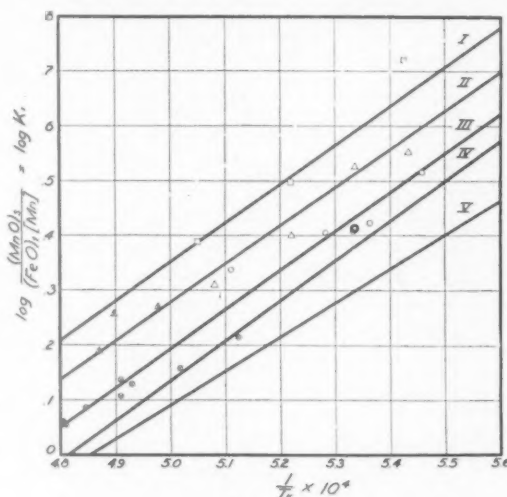


FIG. 1.

Curve Series

A B B/A

I □ < 1.0

II △ 1.0-1.35

III ⊗ ○ > 1.35

IV Pure oxides, Krings and Schackmann.

V Pure oxides, Koerber and Oelsen.

○ Pure oxides, Oberhoffer and Schenck.

the order reversed were found. Finally, when $\log (K_3 \sqrt{R})$ vs. $1/T$ was plotted, a single line resulted (Fig. 3).

Plot of the second form of the manganese equilibrium reaction (Eq. 2) using $\log K_2$ vs. $1/T$ gave a straight line at once (Fig. 4). This is in agreement with the observation that in basic open-hearth slags this ratio is independent of the slag basicity.⁸

Before discussion of the possible significance of these various plots, the data from series A will be considered. For these experiments the optical-pyrometer readings of the slag temperature were entirely without significance. We have, therefore, calculated K_2 from the analytical data of those heats and used these together with Fig. 4 and Eq. 7 to determine the actual temperatures. Temperatures of the series A heats determined in this manner are shown in

Table 1. This function was chosen rather than K_1 or K_3 because it was independent of slag acidity or basicity.

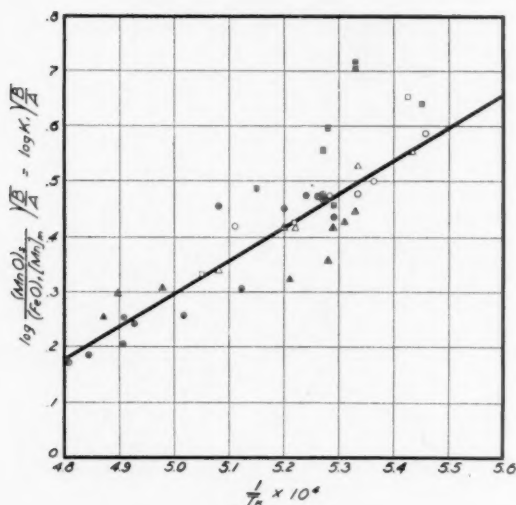


FIG. 2.

Series			
B/A	A	B	Leiber
> 1.35	⊗	○	⊕
1.0-1.35	△	△	△
< 1.0	□	⊠	

Values of K_1 were then computed, and using these calculated temperatures $\log (K_1 \sqrt{R})$ vs. $1/T$ was plotted. These results are included on Fig. 2. It is to be emphasized that the series B results had been studied first, and the line best representing them had been drawn. This line was extended without adjustment of any kind into the region of the series A results, and it was at once evident that a single line was adequate for both series. The line 1 given on Fig. 2 is the least-squares line for all points. It differs little in position or slope from the line originally drawn for the series B points alone.

When the oxygen-distribution coefficient K_3 is calculated and plotted similarly on Fig. 3, the line drawn from the series B results alone did not adequately represent the series A points. It was, however, not far from the line given, which is the least-squares line through all the points.

The least-squares line through all the points (except No. 21, series B) in Fig. 2 is given by the equation

$$\begin{aligned} \log (K_1 \sqrt{R}) &= 5966/T - 2.685 \\ \Delta(1/T) &= \pm 0.038 \\ \Delta T &= 13^\circ \text{ to } 17^\circ \text{C.} \end{aligned} \quad [6]$$

The quantity $\Delta(1/T)$ is the average deviation

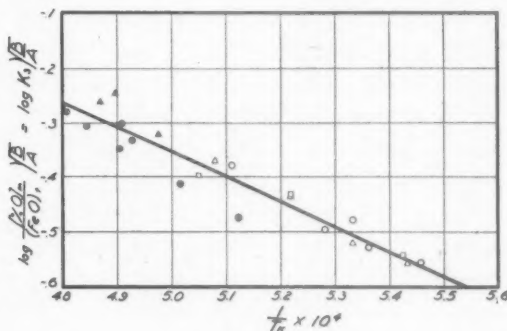


FIG. 3.

Series			
B/A	A	B	
> 1.35	⊗	○	
1.0-1.35	△	△	
< 1.0	□	⊠	

tion of the points from the line. From this the value of ΔT is calculated for the upper and lower limits of the temperature range covered.

The least-squares line through the series B points in Fig. 4 (omitting No. 21, series B) is given by

$$\begin{aligned} \log K_2 &= 10,487/T - 4.592 \\ \Delta(1/T) &= \pm 0.024 \\ \Delta T &= 7^\circ \text{ to } 9^\circ \text{C.} \end{aligned} \quad [7]$$

This is the line used to obtain $(1/T)$ for the series A points.

The least-squares line through all the points of series A and B in Fig. 3 is represented by

$$\begin{aligned} \log (K_3 \sqrt{R}) &= -4510/T + 1.901 \\ \Delta(1/T) &= \pm 0.050 \\ \Delta T &= 16 \text{ to } 21^\circ \text{C.} \end{aligned} \quad [8]$$

The average deviation of the series B points

alone is considerably smaller than for all the points.

In view of the fact that only the plots of Eqs. 1 and 3, which contain $(\text{FeO})_{L.O}$ in the denominator, are simplified by the \sqrt{R} factor, it may be concluded that it is solely, or at least mainly, the activity of the FeO in the slag and not that of the MnO that is seriously affected by the slag acids and bases. For the range of compositions and conditions covered by the experiments reported above, we may therefore write for the activity of the FeO in the slag

$$a_{\text{FeO}} = (\text{FeO})_{L.O} R^{-1/2} = (\text{FeO})_{L.O} \sqrt{\frac{A}{B}} \quad [9]$$

The quantity $R^{-1/2}$ thus becomes the activity coefficient of $[\text{FeO}]_{L.O}$ for this range of compositions and conditions.*

The range of slag and metal compositions in weight per cent covered by equations 6 to 9 is as follows: SiO_2 , 4.8–17.7; CaO , 13.3–45.9; MgO , 4.7–9.8; FeO , 14.1–

65.0; Fe_2O_3 , 2.0–7.6; MnO , 2.1–5.5; P_2O_5 , 0.7–4.1; $\text{O}(\text{in metal})$, 0.05–0.23; $\text{Mn}(\text{in metal})$, 0.01–0.18. The range of $R = B/A = 0.7$ to 1.7 and of $T = 1560^\circ$ to

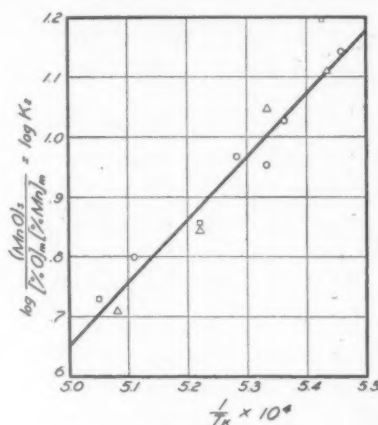


FIG. 4.
Series B Only
 B/A

> 1.35 ○
 $1.0-1.35$ △
 < 1.0 □

* To avoid misunderstanding, it will be well to state just how far we may use such an activity coefficient. Among the ways that this coefficient may be evaluated are: (1) by theoretical means, (2) by direct experimental methods, and (3) empirical methods based on the studies of the equilibria directly concerned. The quantity $R^{-1/2}$ as the activity coefficient for FeO is one of the third class. Like any empirically determined coefficient, its use is justified only for the range of data on which it is based and no further claims are made. That it cannot be universally applicable to all possible slag conditions and compositions may easily be seen by taking some limiting values for R ; viz.,

Assuming			Then R
$\text{SiO}_2 + \text{P}_2\text{O}_5$	CaO	FeO	
0	x	y	∞
x	0	y	0
0	0	z	Indeterminate

The use of $R^{-1/2}$ as the activity coefficient defines a standard state such that $a_{\text{FeO}} = (\text{FeO})_{L.O}$ when $R = 1$. Other standard states may be found, which are either more general or more convenient. In fact, a different one will be used in another article by one of the present authors.

1810°C. The low manganese contents in both metal and slag are to be especially noted.

Because it simplifies the equilibrium relations 1 and 3 over a range of base-acid ratios that has been particularly troublesome to handle, and for which no other means have been found, it is proposed only that the \sqrt{R} factor be used until the experimental results on which it was based are proved to be erroneous or some better method of representation is discovered.

With these restrictions in mind, the use of the \sqrt{R} is a legitimate device in applied thermodynamics and we may obtain from equations 6, 7 and 8 the following expressions for the standard free energy change:

$$\Delta F_1^0 = -27,290 + 12.284T$$

$$\Delta H_1 = -27,290 \text{ cal.} \quad [10]$$

$$\Delta F_2^0 = -47,980 + 21.008T$$

$$\Delta H_2 = -47,980 \text{ cal.} \quad [11]$$

$$\Delta F_3^0 = +20,630 - 8.697T$$

$$\Delta H_3 = +20,630 \text{ cal.} \quad [12]$$

From the three reactions corresponding to Eq. 1, Eq. 2 and Eq. 3, it will be seen that if Eq. 2 is subtracted from Eq. 1 the result is Eq. 3. This permits a check on the three free-energy equations, 10, 11 and 12. Subtracting Eq. 11 from Eq. 10 gives:

$$\Delta F_3^0(\text{calc.}) = +20,680 - 8.724T \quad [13]$$

which is in very satisfactory agreement with Eq. 12. Considering that the constants in Eq. 6, Eq. 7 and Eq. 8 were determined independently by calculating the best lines by the method of least squares, it must be concluded that the results are thermodynamically consistent. A number of other functions were tried—e.g., using $(\text{FeO})_s$ instead of $(\text{FeO})_{L.O.}$, $B = (\text{CaO})_s + (\text{MgO})_s$ instead of $B = (\text{CaO})_s$, but it was considered that the resulting functions were less significant than those given above.

COMPARISON WITH PREVIOUS WORK

The values of the manganese constants found in the basic slags of this investigation do not differ greatly from the previously reported values for slags containing only the oxides of iron and manganese. The average values of K_{Mn} reported by Oberhoffer and Schenck,² Krings and Schackmann³ and Koerber and Oelsen⁴ are shown for comparison in Fig. 1.

It is evident that in each of these investigations the temperature coefficient has been approximately the same and that a general solution of the problem must include the effects of other slag constituents as well as that of temperature. It was pointed out by Tammann and Oelsen¹⁰ that in steelmaking practice the value of K_1 varies from about 2.5 in basic practice to 13 in acid. Krings and Schackmann studied the effects of several added oxides and found that K_1 was strongly increased by silica, decreased by lime and only slightly affected by MgO , Al_2O_3 , CaSiO_3 and Ca_2SiO_4 .

These effects of slag composition are shown graphically in Fig. 5. Curve I is the

line previously drawn by Chipman⁹ to summarize the results on slags containing only $\text{FeO} + \text{MnO}$. Lines II, III and IV are the present authors' results for the three basicity ranges, 1.7 to 1.35, 1.35 to 1, and 1.0 to 0.7. Line V represents the results of Koerber and Oelsen⁴ on silica-saturated slags. The circles and squares represent Krings and Schackmann's results on FeO-MnO slags containing the silica and lime percentages indicated; the triangles, their data on slags containing calcium orthosilicate in alumina and in magnesia crucibles. All of these results apparently represent effects of the added substance upon the activity of FeO or of MnO in the slag.

Comparison with open-hearth operating data is more difficult for several reasons: (1) good open-hearth data including accurate temperature measurements are scarce; (2) even when good measurements are available, there is doubt as to the degree of approach to equilibrium of slag and metal, and a full answer to this question seems beyond the scope of the present paper. In a recent study of slag-metal relationships in the basic open hearth⁸ it was shown that K_1 is virtually independent of the carbon content but varies with the basicity, increasing rapidly as the basicity decreases. The observed values of K_1 were of the same magnitude as those reported herein; the relationship, however, does not involve the square root of the basicity ratio.

The open-hearth studies reported by Leiber¹¹ appear to have been carefully performed and the temperatures were measured thermoelectrically. Excluding results that were obtained soon after a furnace addition, there remain 21 samples in which some approach to slag-metal equilibrium might be expected. These points are plotted in Fig. 1, and not more than half of them lie near the equilibrium line. One of two conclusions may be drawn: that the $\sqrt{B/A}$ relationship does not extend to the type of slag involved or that the condition of the bath does not always reach that required

by the manganese equilibrium. In the slags used by Leiber, the CaO contents were within but on the high side of the range given above, the SiO₂ was in nearly all cases

total iron contents of his slags, so that equation 4 could not be used. By equation 4 all the oxygen in the iron oxides is calculated to FeO while from Leiber's data all the iron

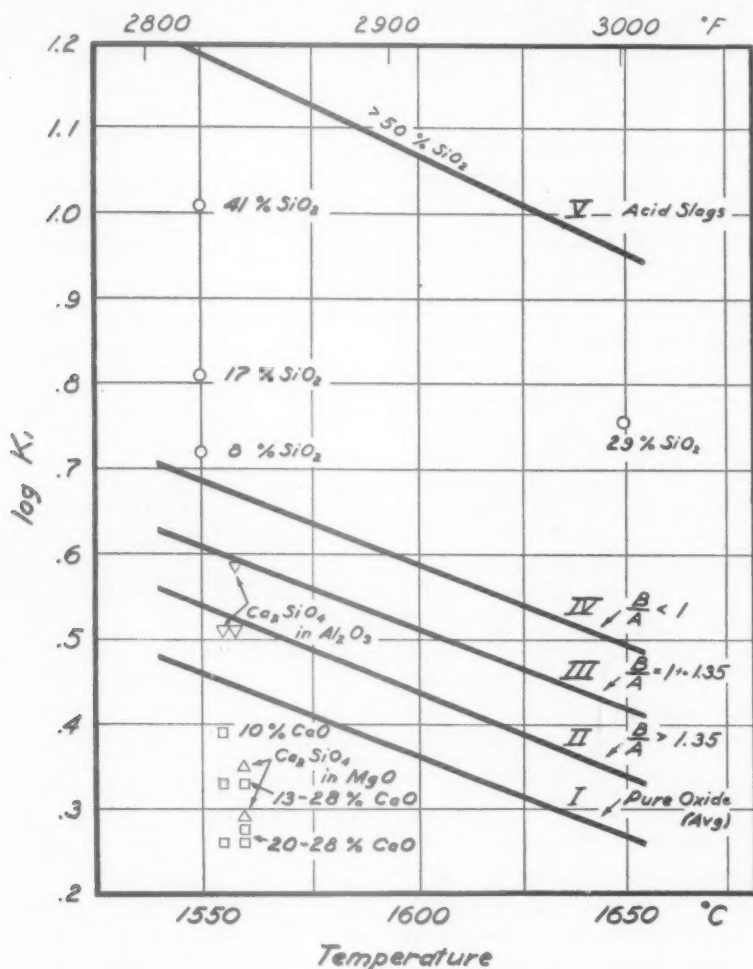


FIG. 5.

Curve or Point

- I Pure oxides (Chipman).
- II Slags $B/A > 1.35$ (present paper).
- III Slags $B/A = 1.0$ to 1.35 (present paper).
- IV Slags $B/A < 1.0$ (present paper).
- V SiO₂ saturated (Koerber and Oelsen).
- FeO-MnO slags, per cent SiO₂ indicated (Krings and Schackmann).
- FeO-MnO slags, per cent CaO indicated (Krings and Schackmann).
- △ FeO-MnO slags + Ca₂SiO₄ in MgO crucible (Krings and Schackmann).
- ▽ FeO-MnO slags + Ca₂SiO₄ in Al₂O₃ crucible (Krings and Schackmann).

well above our limits, the MnO from 2 to 4 times our upper limit, and the FeO well below our lower limit. In addition, it is important to note that Leiber reported the

must be calculated to FeO. This has the effect of making (FeO)_{1.0} too low and thus the constant K_1 too high, but by an unknown amount. In the light of these differ-

ences, it is not in order to speculate further on the relation of Leiber's data to our own. It is worth noting, however, that of the seven points that lie far above the curve in Fig. 3, one or two might be brought into line by reasonable values of Fe_2O_3 contents, while for the other five the ratio of Mn to Fe in the slags is better than 1.5. This far exceeds the corresponding ratio from Tables 1 and 2, which never exceeds about 0.35. This suggests that when the MnO content is high and the FeO low, the activity of the MnO also becomes a function of the slag composition. This is an entirely reasonable behavior and serves to re-emphasize the point already suggested, that in such a complex solution as a slag we cannot expect to represent the activity of any of the various components over wide ranges by simple forms of equations.

ACKNOWLEDGMENTS

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SUMMARY

This paper presents the results of laboratory studies of equilibria involving iron oxide, manganese and manganese oxide between liquid iron and slags of the highly oxidizing basic open-hearth type. The following equilibrium constants were determined:

$$K_1 = \frac{(\text{MnO})_s}{(\text{FeO})_{l.o}[\text{Mn}]_m}; \quad K_2 = \frac{(\text{MnO})_s}{[\text{O}]_m[\text{Mn}]_m};$$

$$K_3 = \frac{[\text{O}]_m}{(\text{FeO})_{l.o}}$$

It was found that K_2 is a function of temperature only, being independent of slag composition.

K_1 and K_3 depend upon temperature and slag basicity. As a measure of the latter, the following ratio of molar concentrations is employed:

$$R = (\text{CaO})_s / (2(\text{SiO}_2)_s + 3(\text{P}_2\text{O}_5)_s)$$

The values of the products, $K_1 \sqrt{R}$ and $K_3 \sqrt{R}$ are simple functions of temperature for all the slags studied.

Little comparison with published open-hearth data was possible and that only for $K_1 \sqrt{R}$. Even the most satisfactory of the published data were not strictly comparable, but about half of the points fell on the calculated curve.

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DISCUSSION

(C. H. Herty, Jr., presiding)

A. L. FIELD,* Baltimore, Md.—It seems to me that the authors have extracted about as much as could possibly be obtained from the experimental data in hand. It is particularly unfortunate, however, that so elaborate and careful a study is based upon slag and metal samples exhibiting such a small variation in Mn and MnO content. It is to be hoped that such studies will be extended to open-hearth

* Rustless Iron and Steel Corporation.

steels containing Mn contents above 0.0236 per cent.

In first glancing through this paper I was somewhat confused at the use of the symbol

percentage of FeO_x the activity of iron oxide passes through a maximum at or near the point corresponding to two mols $\text{CaO} + \text{MgO}$ to one SiO_2 . Thus, according to the authors of the

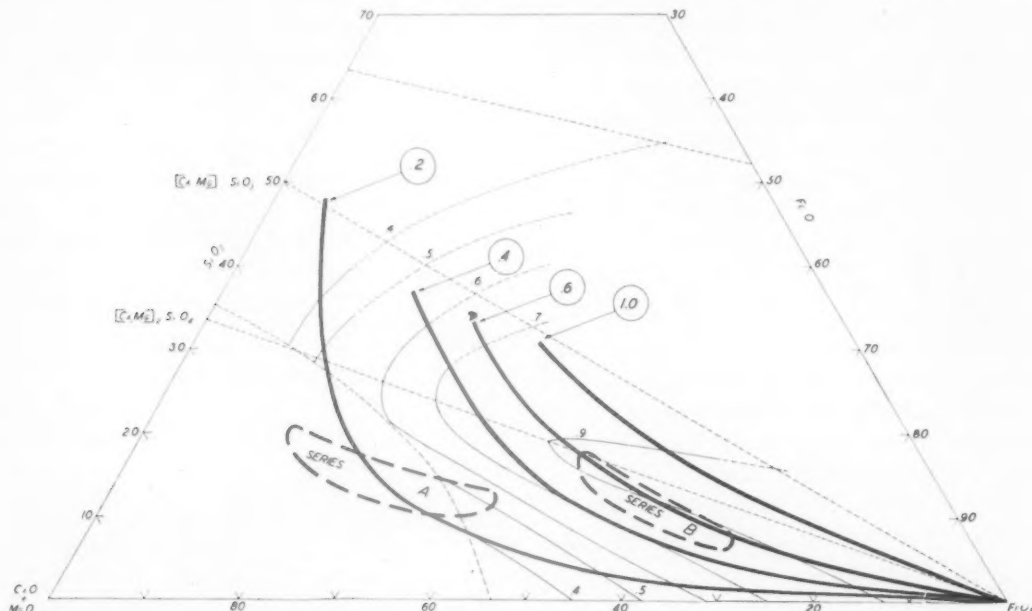


FIG. 6.—ACTIVITY OF IRON OXIDE IN SLAGS, PLOTTED ON A MOL-FRACTION BASIS.

Isoactivity curves as calculated from the relation given by Jette, Ellis and Chipman are shown heavily superimposed on the diagram given by Fettes and Chipman.

R with a thermodynamic equation where this symbol does not refer to the gas constant, as is usual. It might be well to use a different symbol for the empirical oxide component ratio of equation 5.

L. S. DARKEN,* Kearny, N. J.—It is of interest to compare the activities of FeO as derived in this paper with those obtained by Fettes and Chipman (this volume, p. 95). Although the two systems are not identical, it seems reasonable to suppose that the relatively small amounts of MnO , P_2O_5 and S occurring in the slags of the present investigation have but little effect on the activity of FeO . If this be granted, the activities as given in the two papers may be directly compared.

The conclusion reached by the authors that the activity of FeO is given by the expression

$a_{\text{FeO}} = (\text{FeO})_{l,0} \sqrt{\frac{A}{B}}$ appears to be at variance with the findings of Fettes and Chipman, who show (Fig. 6) that at constant

present paper, the activity of FeO always increases (in the region investigated) with increasing values of A/B whereas the data of Fettes and Chipman appear to indicate that the activity increases with increasing values of A/B only up to $A/B = 1$ and then decreases. However, this discrepancy is not as large as it first appears, since Fettes and Chipman have grouped CaO and MgO together as a single component whereas the present authors consider only CaO (and not MgO) as a base in the B term of the ratio A/B .

The comparison is shown in Fig. 6 (above). This figure was prepared by superimposing isoactivity lines calculated from the relation $a_{\text{FeO}} = (\text{FeO}) \sqrt{\frac{A}{B}}$ on Fig. 4 of Fettes and Chipman's paper; MgO solubility was taken from Fettes and Chipman. The approximate zones (reduced to 100 per cent $\text{CaO} + \text{MgO} + \text{SiO}_2 + \text{FeO}$) covered by series A and B of Jette, Ellis and Chipman are designated. Inside zones A and B the two sets of isoactivity lines may be regarded as sufficiently parallel for

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practical purposes; however, the absolute values and even the relative values (allowing for the difference in the standard state) differ considerably.

It is worth noting that the data of Jette, Ellis and Chipman cover not a single range but rather two distinct and isolated ranges, not only in regard to composition but also in regard to temperature. It has been pointed out frequently that data distributed in such a nonrandom fashion is not susceptible to statistical correlation; and yet this is just what the authors have done in using an empirical relation with admitted stringent limitations. The authors point out that their relation is empirical and is intended to apply only in the range covered. Even if it be granted that the method of expressing the results is sufficiently precise in the zones investigated, the limitation imposed seriously limits application to open-hearth procedure.

The expression used for the activity of FeO ($a_{\text{FeO}} = (\text{FeO})_{\text{L.O}} \sqrt{\frac{A}{B}}$) implies no single standard state ($a_{\text{FeO}} = 1$) such as unit mol fraction FeO, but rather a continuous series of equivalent standard states at all points where $(\text{FeO})_{\text{L.O}} \sqrt{\frac{A}{B}} = 1$, as shown in Fig. 6. These are physically unattainable states, since the activity of a substance in solution cannot be equal to or greater than the activity of the pure molten substance.

The authors express the results as free-energy equations; these, of course, are expressions for ΔF° , the free-energy change accompanying a reaction in which all reactants and products are in their standard states. The standard state, or rather the standard states, are all outside the range of investigation; the expressions used are not valid in the vicinity of standard states. The authors even point out that their expression yields an indeterminate value for a_{FeO} in the case of pure iron oxide in equilibrium with metallic iron. Hence ΔF° and ΔH of this paper are not free-energy and heat changes accompanying the reactions of pure reactants to yield pure products but rather the free-energy and heat changes accompanying reactions in which at least one of the products or reactants is in a physically unattainable state. The use of such a fictitious

standard state is certainly a permissible procedure, which is used frequently; e.g., in dilute aqueous solutions. However, it is apt to be quite misleading since ΔF° does not apply to any real reaction and the ΔH obtained therefrom applies not to pure components but to the compositions investigated. Moreover, since the empirical expression used is not strictly valid, errors of uncertain magnitude are introduced; these errors are apt to be multiplied many times in calculating values of ΔH .

In general it seems undesirable to use an empirical expression that does such violence to limiting conditions, even when the limitations are clearly stated.

E. R. JETTE (author's reply).—The low manganese contents mentioned by Mr. Feild is called to the reader's attention in two places in the paper.

The authors are grateful to Dr. Darken for discussing matters that were omitted largely for the sake of saving space. Dr. Darken's remarks concerning the use of the ΔF° and ΔH values are, of course, quite correct; precisely the same warnings are necessary whenever empirical equations representing experimental data are introduced into thermodynamic treatments. In such empirical treatments, however, it is not of vital importance whether the standard states are outside the range of the experiments or even fictitious, as long as these are clearly understood. In connection with Dr. Darken's Fig. 6, it should be noted that in the areas representing series A and B, the composition differences giving rise to the separation resulted mainly from the different temperature ranges of the two series. In series B the temperature range averaged 1625°—i.e., not far from the temperature 1600°C. corresponding to Fig. 4 of Chipman and Fettters—while the series A temperatures averaged 1760°C. This probably accounts for part of the difference Dr. Darken discusses.

The authors have no illusions that Eq. 9, defining the activity of FeO in the slag, and Eqs. 10, 11 and 12, giving the free energy and heat-content changes, are necessarily correct for other conditions and, as Dr. Darken recognizes, have been careful to state the limitations. By Eq. 9 it was, however, possible to bring the experimental results into some sort of order.

Equilibria of Liquid Iron and Slags of the System CaO-MgO-FeO-SiO_2

BY KARL L. FETTERS,* JUNIOR MEMBER, AND JOHN CHIPMAN,† MEMBER, A.I.M.E.

(New York Meeting, February 1941)

THE relationship between the composition of the slag and that of the underlying metal during the refining of a heat of liquid steel may best be studied in the light of the two broad physicochemical concepts of equilibrium and reaction rate. Actual steel-making processes, typified by basic open-hearth practice, involve such complexities of operating variables that it is impossible to distinguish with any degree of certainty between the general limiting conditions imposed by chemical equilibrium and the effects associated with rates of diffusion or of chemical reaction. Further advances in the physical chemistry of steelmaking will depend upon our ability to distinguish clearly between these two kinds of effects, and the experimental work that must be done falls naturally into two classifications. The first is the study of chemical equilibrium that cannot be carried out with assurance under operating conditions but must be done in the laboratory. The second is the subject of rates of reaction and diffusion and the mechanism of the process as a whole, which can best be studied under operating conditions. The latter is not entirely independent of the former, since its interpretation often requires a knowledge of the equilibrium state. It is the purpose of this and of several papers that will follow to present the results of labora-

tory investigations of equilibria involving liquid steel and slag.

Open-hearth slag is a complex mixture containing at least eight major components and perhaps twice as many whose influence may be classified as probably minor. It is not surprising that progress toward a complete understanding of such a material at high temperatures has been slow. Attempts to apply the established principles of physical chemistry to the behavior of the individual components of this mixture have been beset by an almost complete lack of data on its chemical properties in the liquid state. This has necessitated the adoption of various methods of approximation based upon such assumptions as, for example, that for a given component the ratio of its mol fraction in the slag to that in the metal is a constant, or that the molecular composition of the liquid slag is the same as its crystalline constitution after solidification. From the thermodynamic viewpoint, such assumptions are merely useful dodges, which enable one to hazard a guess as to the magnitude of the more fundamental quantities, the chemical potentials and activities of the components of slag.

The problem of determining the activity of each substance in an eight-component system seems too complex to be undertaken without the aid of generalizations derived from experimental data on similar systems containing a smaller number of components. Accordingly, it was planned in the present investigation to study the equilibrium of molten iron with the simplest

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possible slag that would in any way resemble open-hearth slag. It was hoped that the results obtained might serve as a guide to future studies of the more complex systems.

The three essential components of basic slags are lime, silica and iron oxide, but for practical reasons it was not possible to restrict the study to a three-component system. Iron oxide is not a simple compound and therefore must be regarded as two components, specifiable either as Fe and O or more conveniently as FeO and Fe₂O₃. The experimental work was carried out in magnesia crucibles, thereby adding a fifth component to the system.

EXPERIMENTAL METHOD

The induction furnace used in this investigation and the experimental methods employed have been described elsewhere.^{1,2} The important features of the method may be summarized briefly as follows: A 65-lb. melt of ingot iron in a magnesia crucible was vacuum-treated to reduce its carbon content to about 0.005 per cent. A synthetic slag was added in an amount sufficient to cover the metal completely. A graphite heater block an inch or two above slag level prevented chilling of the surface. A nitrogen atmosphere was maintained. Temperatures were measured with tungsten-molybdenum thermocouples. Slag and metal samples were secured by dipping small steel molds into the bath. The time allowed for attainment of equilibrium after any addition or change in temperature was at least 30 min. This was based upon the experimental finding that the oxygen content of the bath attained a steady value within 18 to 23 min. after additions of either iron oxide or ferrosilicon.

RESULTS

During the course of this investigation 22 heats were made, from which 170 slag samples and a larger number of metal tests

were secured, most of them at definitely determined temperatures. Space does not permit the publication of a full record of each heat, but the clock times and the analytical results are given in Table 1. The record of a part of one of these heats, involving only the solubility of FeO under simple iron oxide slags, has been shown elsewhere.²

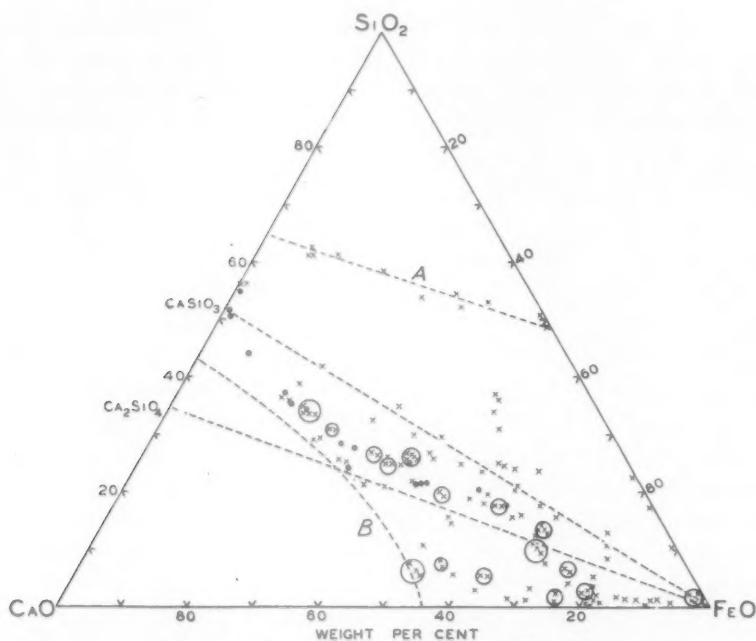
The compositions of the slags are shown in the ternary diagram of Fig. 1. In order to represent a five-component system on a triangular diagram, some simplification obviously is needed. For the present purpose this has been accomplished by ignoring MgO and by computing the total iron content of the slag as FeO. This method of recording the iron oxide content was used by Bowen, Schairer and Posnjak³ in their study of the lime-silica-iron oxide system at temperatures up to 1500°C. It is also commonly employed in many open-hearth plants and will be used repeatedly in this paper under the designation FeO_t.

The larger circles in the diagram represent groups of slags very similar in composition but obtained at quite different temperatures, which were used to establish the temperature coefficients of the several relationships that will be discussed in the sequel. The lines bordering the fields at the SiO₂ and CaO corners represent the approximate limits of solubility of the solid phases at 1600°C.

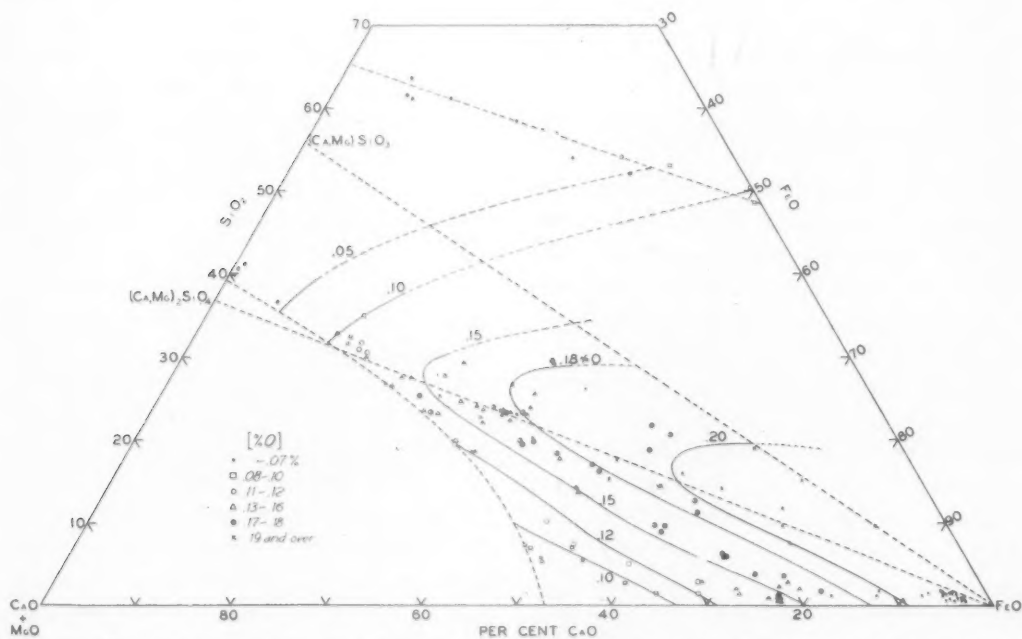
Distribution of Iron Oxide between Slag and Metal.—One of the principal objects of this investigation was to determine the effect of slag composition on the equilibrium oxygen content of the metal. The effect of temperature upon the solubility of iron oxide in iron under nearly pure iron oxide slags has been shown in a previous paper² to be capable of representation by the formula (temperature in degrees Kelvin):

$$\log \text{ per cent oxygen} = -4860/T + 1.935 \quad [1]$$

¹ References are at the end of the paper.

FIG. 1.—TERNARY SYSTEM CaO-FeO-SiO_2 .

Lines A and B, approximate limits of liquid slag compositions at 1600°C . Points indicated by X, experimental slags sampled at accurately measured temperatures; ● at estimated temperatures. Larger circles show groups used to establish effects of temperature.

FIG. 2.—OXYGEN CONTENT OF METAL AT 1600°C . IN EQUILIBRIUM WITH SLAGS OF SYSTEM $(\text{CaO} + \text{MgO}) - \text{FeO} - \text{SiO}_2$.

It was found that for each of the slag groups of Fig. 1 the oxygen solubility in the metal could be represented by a similar equation whose slope was (within the sometimes wide limits of experimental error) the same for all groups. This provided a method for correcting to a round temperature of 1600°C. all data secured between 1550° and 1650°C.

In this way the oxygen content of the metal in equilibrium with each of the slags represented in Fig. 2 has been corrected to 1600°. Lines are drawn between these points to divide the field into regions of several oxygen ranges, each line being the projection of an iso-oxygen contour. In preparing Fig. 2, the FeO of the slag was again computed from the total iron content. CaO and MgO were taken together as one component of the slag, simply by adding their weight percentages. It is not intended to imply that these oxides are equivalent, weight for weight. This is simply used as an empirical means of reporting the data.

The distribution ratio for iron oxide defined by the equation

$$L_0 = [\% \text{ oxygen}]/(\% \text{ FeO}_i)$$

is shown in Fig. 3. Again the points represent slag compositions calculated to the ternary basis mentioned above and the lines are drawn to divide the field into regions representing small ranges in the value of L_0 .

Certain regions of the diagram contain no experimental points. Because of the high solubility of magnesia in the more acid slags, it was impossible to hold in the magnesia crucible slags more acid than those on the FeO-metasilicate join. The portion of the diagram lying between this line and the silica-solubility line could not be studied by the method employed. The broken lines drawn through this region are therefore entirely hypothetical and represent only one of the possible interpretations

of the data. Attention is called to the result that L_0 is by no means constant.

Activity of FeO in Slag.—Since it has been demonstrated in an earlier investigation⁴ that the activity of iron oxide in liquid iron is proportional to its concentration, the new data permit an evaluation of its activity in the slags. For this purpose the reference state, in which the activity of FeO is unity, will be taken as pure iron oxide (not pure FeO) in equilibrium with iron. The composition of this oxide² at 1600° is approximately 6 per cent Fe_2O_3 , 94 per cent FeO, which corresponds to the empirical formula $\text{FeO}_{1.03}$.

In order to treat the iron oxide of the slag as a single component in plotting diagrams on a mol-fraction basis, it will be convenient to represent the iron oxide of the equilibrium slag by the formula FeO_x , the value of x depending upon temperature and composition. This formula does not represent an actual molecule, nor is it possible at this time to state what molecular species are present in the slag. Analytical results are generally calculated as FeO and Fe_2O_3 , but with equal reason might be reported as FeO and Fe_3O_4 or the ions Fe^{++} , Fe^{+++} and O^{--} . It is not necessary to know the molecular constitution of the liquid in order to obtain a sound thermodynamic treatment of the equilibrium data. For the sake of clarity it is assumed that the oxidizing agent in the slag is FeO and accordingly the activities to be computed are assigned to that oxide. The results, however, will represent the *oxidizing activity* of the slag whether or not the oxidizing agent is actually FeO.

A study of Figs. 2 and 3 reveals the interesting fact that as the FeO corner of the triangle is approached the oxygen content of the metal becomes relatively insensitive to variations in slag composition. It seems probable, therefore, that the saturation value for oxygen in iron under pure FeO_x will be only slightly greater than the oxygen content of the metal under

slags containing 90 to 96 per cent total FeO. For purposes of calculation this is taken as 0.23 per cent oxygen at 1600°. The activity of FeO in any slag at this

1550° and 1650° were corrected to 1600° by means of approximate temperature coefficients based upon data covering a wider range of temperatures. The results

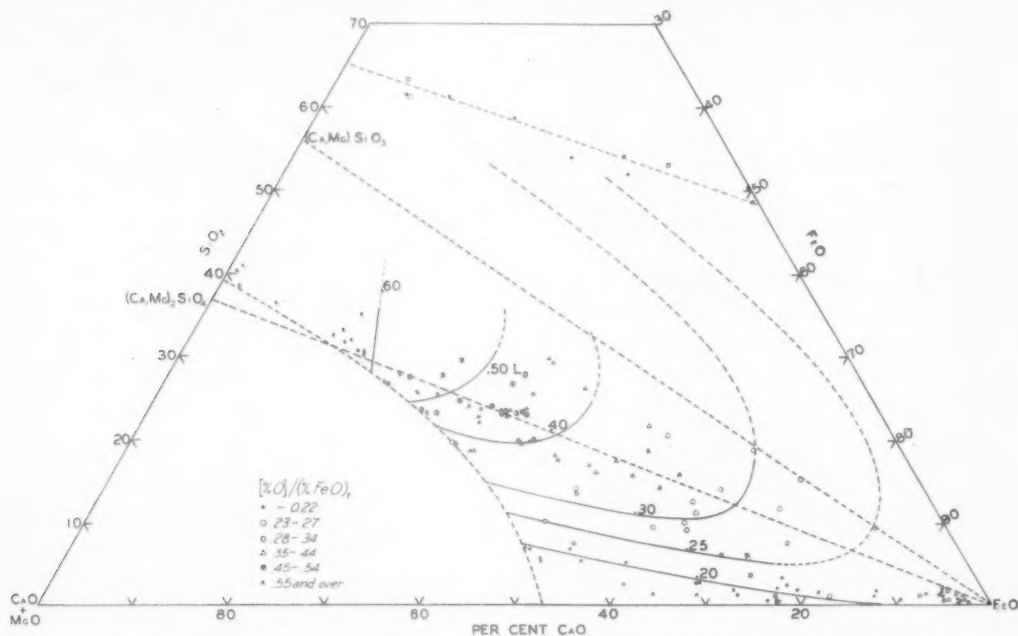


FIG. 3.—DISTRIBUTION RATIO AT 1600°C. OF OXYGEN BETWEEN SLAG AND METAL.
 $L_0 = [\% \text{O}]/(\% \text{FeO}) \text{ TOTAL.}^*$

temperature is then obtained by dividing the oxygen content of the equilibrium metal by 0.23.

The results are presented in Fig. 4, where the activity of FeO is shown as a function of mol fractions in the quasi-ternary system $\text{FeO}_x\text{-SiO}_2\text{-(CaO + MgO)}$. It is of interest to note that while the calculations were based upon a temperature of 1600°, the final result shown in Fig. 4 is applicable, within the limits of our experimental error, to any temperature within the range of the experiments. This follows from the definition of activity as the ratio of the oxidizing power of the slag to that of pure FeO_x and the observation previously noted, that for slags of constant composition the temperature coefficient of the distribution ratio is the same for all slags (acid slags possibly excepted).

Ferric Oxide in the Slag.—The ferric oxide contents of all slags taken between

are shown in Fig. 5. Several features of this diagram are worthy of note. In the first place, it is observed that all of these slags contain Fe_2O_3 therefore it is no longer permissible to assume that all of the ferric oxide is reduced to ferrous by contact with the metal. Rather, it is reduced to the equilibrium concentration shown in Fig. 5, in which the ratio $(\text{Fe}_2\text{O}_3)/(\text{FeO})$ is substantially lower than in open-hearth slags. The ferric oxide is decreased by increasing silica and is increased by increasing lime. The effect of temperature was not accurately established but in general it was found that higher temperatures produced slightly lower concentrations of Fe_2O_3 . Our data at 1600° are in very good agreement with the diagram for slightly lower temperatures published by Bowen, Schairer and Posnjak.³

* See correction on page 111, second column.

Solubility of Magnesia in Slag.—All of the basic slags contained magnesia, a large part of which was in true solution in the slag. Evidence that it was not merely held in suspension is found in the following observations:

1. Samples of slag representing widely

spaced parts of the system were subjected to careful petrographic examination and in none of them could periclase be found.

2. After the heat had been molten for an hour or two, no further increase occurred in magnesia content except as a result of changes in temperature or slag composition.

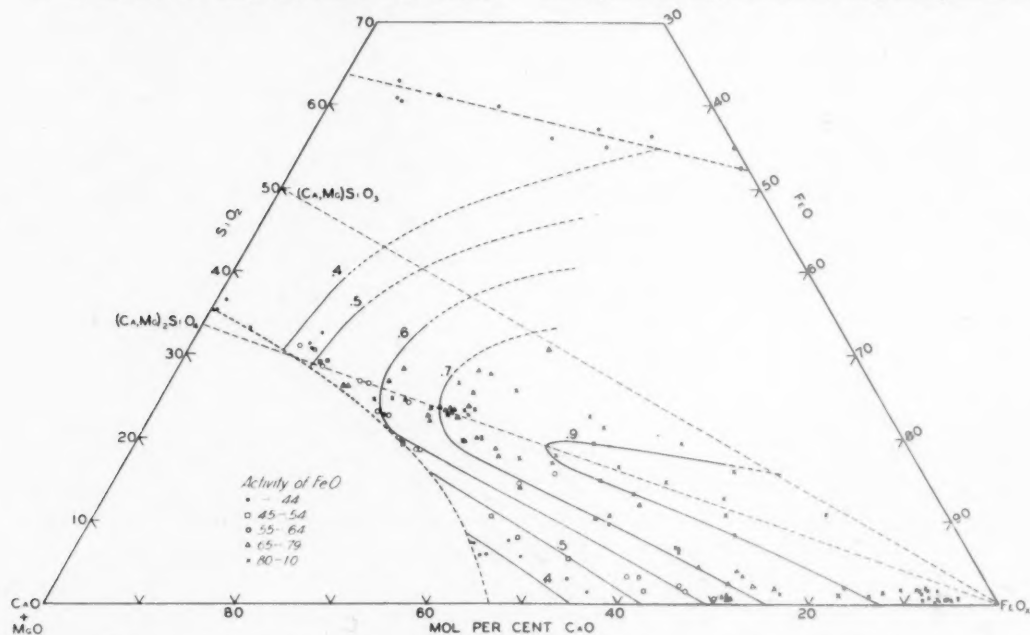


FIG. 4.—ACTIVITY OF IRON OXIDE IN SLAGS, PLOTTED ON A MOL FRACTION BASIS.

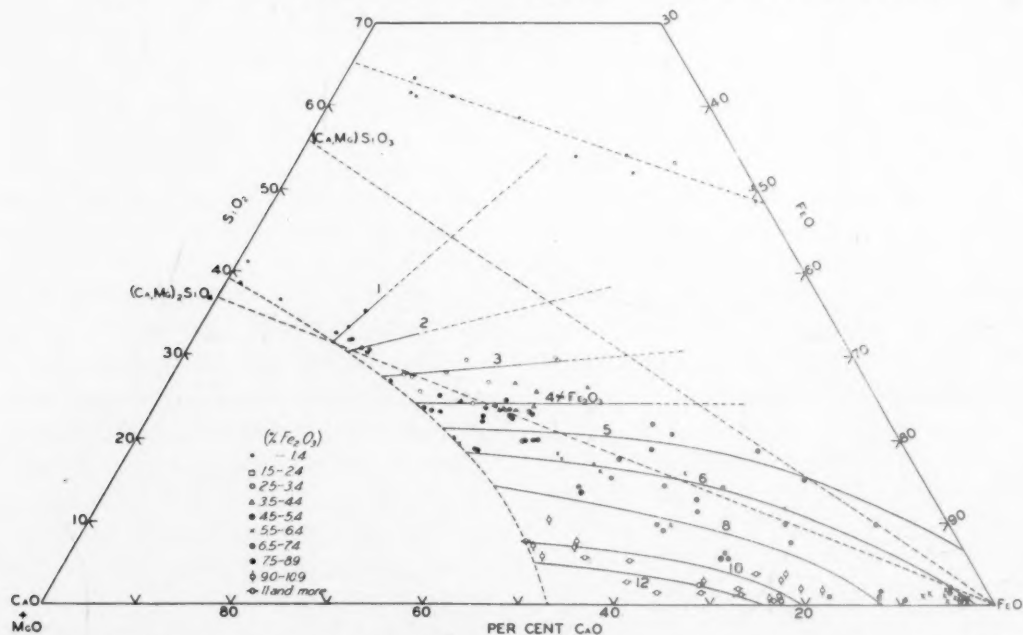


FIG. 5.—PERCENTAGE OF FERRIC OXIDE IN SLAGS IN EQUILIBRIUM WITH LIQUID IRON AT 1600°C.

3. The magnesia content varied rather regularly with the temperature, frequently decreasing when the temperature was lowered, as though it had been precipitated upon the crucible wall.

4. It also varied in a regular manner with the chemical composition of the slag, as will be shown presently.

For these reasons, it seems probable that the analytical results represent, at least approximately, the solubility of MgO in the slags. The possibility of undersaturation or of the presence of some suspended magnesia must be recognized as detracting from the precision of the results, but careful study of the data has led us to conclude that the errors from these sources are generally small.

The solubility of magnesia in the nearly pure iron oxide slags is shown in Fig. 6, in which the logarithm of the percentage of MgO is plotted against the reciprocal of absolute temperature. With the exception of two points, which are noticeably out of control, the data fall within a reasonably narrow band. Slags containing more than 1 per cent SiO_2 are designated by a special symbol and these points fall slightly above the others. The line is drawn in such a way as to give greater weight to the points of lower silica content. Its equation is

$$\log \% \text{MgO} = -6600/T + 4.02 \quad [2]$$

The other slag groups of Fig. 1 gave lines approximately parallel to this and from the average slope it was possible to correct all of the solubility data between 1550° and 1650° to a comparison temperature of 1600° . The results were plotted in Fig. 7 and lines of equal magnesia content were drawn. A large proportion of the observations lie within the range of magnesia contents observed in open-hearth slag. This strongly suggests that in these slags also the magnesia is largely in solution.

Distribution of Sulphur between Slag and Metal.—The distribution ratio, defined by the equation,

$$L_s = (\% \text{S})/[\% \text{S}]$$

is a useful criterion of the desulphurizing power of the slag. This ratio was determined by analysis of many of the slag and metal

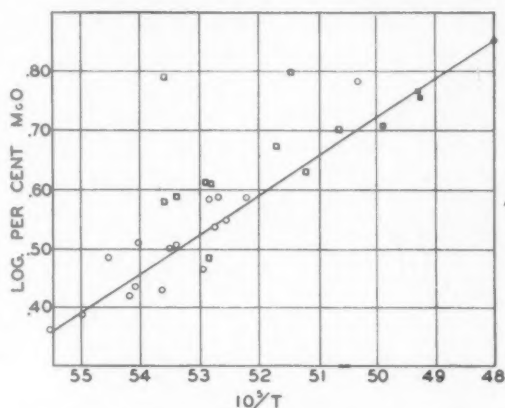


FIG. 6.—SOLUBILITY OF MAGNESIA IN LIQUID IRON OXIDE AS FUNCTION OF TEMPERATURE. Squares indicate slags containing more than 1 per cent SiO_2 ; circles less than that amount.

samples. The original sulphur content of the metal was less than 0.025 per cent, and this was increased to about 0.08 in some heats by addition of iron sulphide. It was found, however, that the high sulphur had a marked tendency to retard analysis of the gases evolved in the vacuum-fusion analysis of the metal for oxygen and for this reason most of the heats were kept below 0.04 per cent S.

The sulphur distribution ratio proved to be rather insensitive to temperature and the results obtained between 1550° and 1650° were therefore plotted without correction. The ternary diagram showing the variation of this ratio with slag composition is given in Fig. 8. The magnitude of this ratio and its general trend with composition are very strikingly similar to the general behavior of sulphur in the open hearth. Any quantitative comparison must await a determination of the effects of manganese and phosphorus upon the equilibrium.

Molecular Constitution of the Slags.—The symmetry of Figs. 2, 3 and 4 with respect

to the line joining FeO with the orthosilicate suggests that the latter may be one of the important molecular aggregates of the slag. A considerable number of the slags were near enough to this line to warrant their treatment as members of the quasi-

binary system $\text{FeO}_x\text{-(CaMg)}_2\text{SiO}_4$. For the group lying within ± 5 per cent of this line in Fig. 4, the mol fractions of these two components was plotted against the activity of FeO as shown in Fig. 9b. The best line through the points of this plot deviates

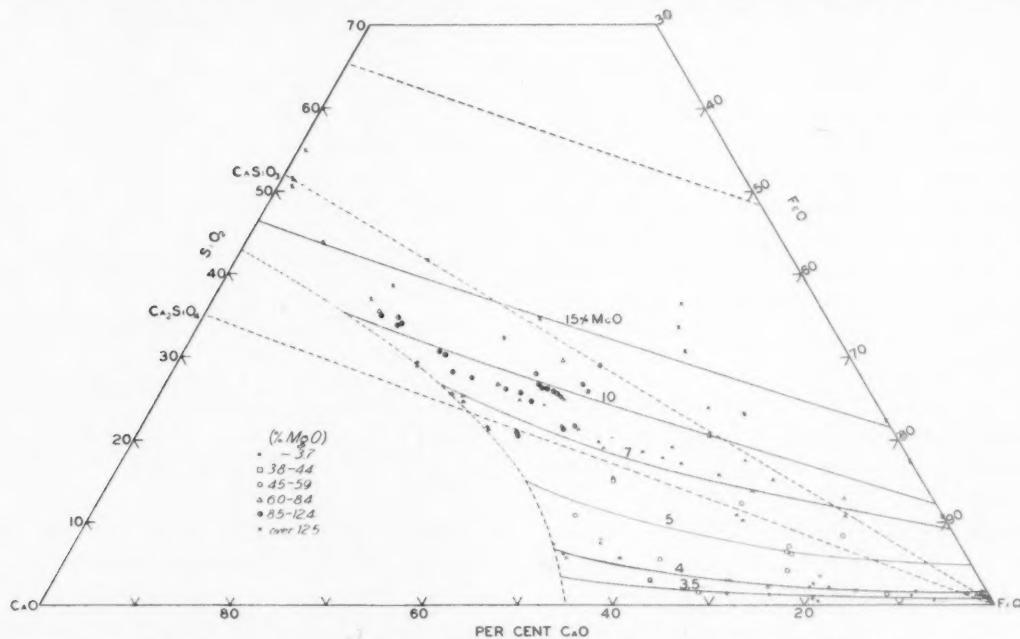


FIG. 7.—SOLUBILITY OF MAGNESIA IN CaO-FeO-SiO_2 SLAGS AT 1600°C .

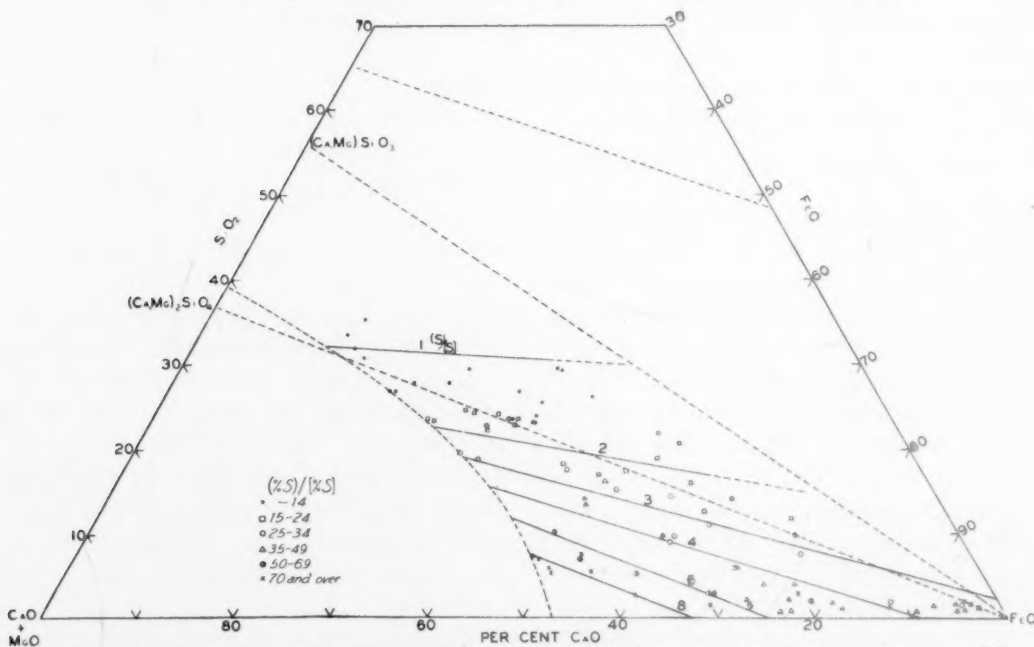


FIG. 8.—DISTRIBUTION OF SULPHUR BETWEEN SLAG AND METAL IN RANGE 1550° TO 1650°C .
 $L_s = (\% \text{ S})/[\% \text{ S}]$.

somewhat from the straight line predicted by Raoult's law. Whether this deviation is due to a wrong choice of molecular formulas or to mere nonideality of the

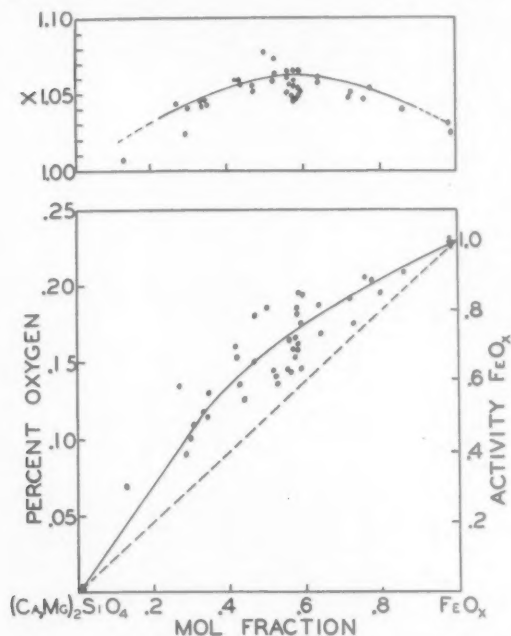


FIG. 9.—OXYGEN IN METAL AS FUNCTION OF SLAG COMPOSITION IN SYSTEM $\text{FeO}_x\text{-Ca}_2\text{SiO}_4$.

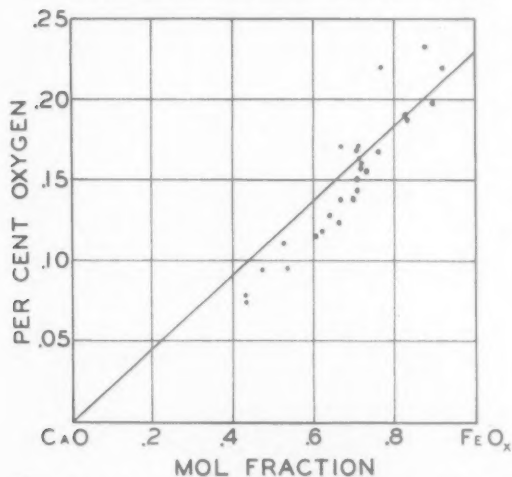


FIG. 10.—OXYGEN IN METAL VERSUS MOL FRACTION FeO_x IN SLAG SYSTEM FeO-CaO .

solution, cannot be decided at the present time. Fig. 9a shows the observed value of x in the constituent FeO_x of this group of slags.

The nearly silica-free slags throw some light on the constitution of the simple lime-

iron oxide system. A plot of the oxygen content of the metal against the mol fraction of FeO_x in the system CaO-FeO_x is shown in Fig. 10. Near the FeO end the

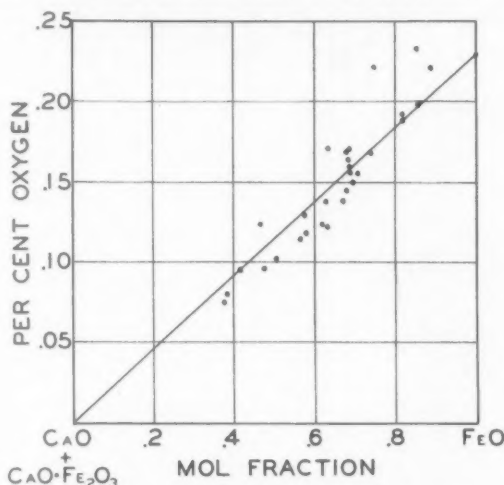


FIG. 11.—OXYGEN IN METAL VERSUS MOL FRACTION FeO IN SLAG SYSTEM $\text{FeO-CaO-CaO-Fe}_2\text{O}_3$.

agreement with the straight line representing Raoult's law is fairly good but with higher percentages of lime a considerable divergence occurs. Again the discrepancy could be ascribed to nonideality of the solution, but a more satisfying explanation can be had on the basis of the formation of stable calcium ferrites in the slag. The same data were recalculated to a basis of mol fraction of FeO in slags containing CaO and $\text{CaO-Fe}_2\text{O}_3$. As shown in Fig. 11, the great majority of the points now fall quite close to the straight line.

A more detailed study of the molecular (or ionic) nature of the slag must be deferred to a later paper.

SUMMARY

This paper presents the results of an experimental study of equilibrium between slags and liquid iron at temperatures used in steelmaking. To simplify interpretation of results, the simplest mixture that would be comparable to open-hearth slag was employed, consisting of CaO , MgO , SiO_2 , FeO and Fe_2O_3 .

TABLE I.—Summary of Experimental Data

Heat	Steel Test	Clock Time	Temperature, Deg. C.	In Metal		In Slag						
				S	O	CaO	SiO ₂	FeO	Fe ₂ O ₃	FeO Total	MgO	S
E-3.....	1	2:40	1795	0.022	0.235	20.78	15.75	47.89	5.13	52.51	10.00	0.04
	4	3:15	1630	0.023	0.213	21.97	17.37	46.85	5.31	51.63	8.43	0.04
	6	4:40		0.025	0.141	22.91	18.25	44.27	5.58	49.30	7.74	
	8	5:00		0.025	0.135	22.82	18.15	44.05	5.46	48.97	7.64	
E-4.....	1	11:30		0.023	0.192							
	2	1:38	(1620) ^a	0.023	0.152	39.96	23.02	25.75	4.55	29.85	6.60	
	5	2:37	1620	0.023	0.143	40.63	23.44	24.23	4.43	28.21	6.98	
	6	3:14	1613	0.024	0.188	39.46	23.09	24.98	4.50	29.08	7.43	
	8	4:32	1598	0.023	(0.153)	41.89	26.55	20.38	2.97	23.05	7.52	
	11	4:52	(1600)	0.023	(0.161)	41.71	26.50	19.54	3.46	22.66	7.72	
E-5.....	1	12:48	1538	0.023	0.112	39.00	29.84	18.60	2.26	20.64	9.23	0.03
	3	1:45	(1505)	0.105	0.105	40.18	30.30	16.76	2.05	18.60	9.51	
	5	2:50	1593	0.022	0.107	42.05	31.54	15.02	1.76	16.60	8.81	0.03
	7	3:22	1602		(0.103)	41.73	31.73	14.77	1.49	16.11	9.84	
	9	4:28	1546	0.022	(0.121)	40.55	30.23	17.85	2.28	19.90	8.85	0.03
	11	5:25	1575		0.120	40.02	30.06	16.94	2.16	18.88	10.59	
	13	5:55	1575	0.025	(0.109)	39.22	30.20	16.11	2.01	17.92	10.81	0.03
E-6.....	1	3:17			0.174							
	2	6:26	1550	0.021	0.112	35.70	18.85	30.96	5.33	35.76	9.31	0.05
	4	6:46	1552		0.112	35.69	18.89	31.52	4.97	35.99	9.14	
	6	7:50			0.110	38.52	19.76	27.83	5.92	33.15	7.65	
	8	8:15		0.020	0.119	38.65	19.59	28.23	5.60	33.27	7.68	0.05
E-8.....	1	10:35			0.176							
	2	10:55			0.198							
	3	1:43	(1570)		0.154	30.35	19.71	36.42	5.62	41.48	7.70	
	5	2:44	(1570)		0.171	30.18	19.82	36.74	5.58	41.76	7.61	
	7	3:49	(1570)		0.158	30.99	19.24	35.13	4.99	39.62	7.79	
	10	4:05	1577	0.014	0.165							
E-9.....	1	9:27			0.265							
	2	10:41	(1540)		0.154	37.41	25.28	24.67	4.96	29.13	7.75	
	4	11:40	(1540)		0.149	38.41	25.50	23.68	3.47	26.80	8.62	
	6	12:24	(1540)		0.112	41.01	32.57	13.05	1.58	14.47	11.46	
	8	12:35	(1540)		0.042							
	9	1:23	(1540)		0.057	40.90	37.06	6.38	0.16	6.52	16.65	
	11	2:19	(1540)		0.009	39.13	41.48	1.06	0.04	1.10	19.28	
	13	3:03	(1540)		0.0022	37.02	40.36	0.57	0.08	0.64	22.95	
	15	3:50	(1540)		0.0033	32.65	40.58	0.39	0.20	0.57	26.20	
	17	4:44			0.0030	30.77	39.20	0.35	0.08	0.42	27.81	
	19	6:47		0.018	0.0027	28.83	37.43	0.57	0.24	0.79	29.77	
E-10.....	1	10:22			(0.253)							
	2	11:01			0.266							
	3	11:36	1565	0.023	0.157	29.80	22.92	34.95	4.83	39.30	6.89	0.03
	5	12:19			0.166	29.92	22.98	34.50	4.50	38.55	7.93	
	7	2:32	1571		0.170	29.57	23.10	32.48	3.83	35.93	9.79	
	9	3:00	1601		0.168	29.33	22.92	33.00	4.00	36.00	9.44	
	11	3:30	1596	0.024	0.155	29.63	22.96	32.40	4.50	36.45	9.19	0.04
	13	4:18	(1575)	0.054	0.150	29.92	23.16	32.85	4.75	37.12	8.59	0.08
	15	4:46		0.056	0.143	30.04	23.12	32.51	4.80	36.83	8.83	0.08
	17	5:28		0.055	0.154	30.48	23.60	31.53	4.05	35.17	9.04	0.08
E-11.....	1	10:26			0.247							
	2	11:51			0.139							
	3	12:24			0.145							
	4	1:15	1556	0.034	0.110	38.06	27.32	22.13	3.25	25.05	8.88	0.05
	6	2:16	1581		0.128	38.73	27.54	21.15	3.17	24.01	9.10	
	8	2:31	(1590)		0.140	33.55	23.48	30.30	4.67	34.50	8.03	
	10	2:39			0.278							
	11	2:56	1594	0.034	0.142	35.07	24.30	27.87	4.03	31.50	7.92	0.06
	13	3:07		0.077	0.136							
	14	3:21		0.077	0.122							
	15	3:53		0.078	0.126							
	16	4:14		0.077	0.125	35.36	24.38	27.50	4.27	33.36	7.90	0.12
	18	4:44		0.075	0.133							
	19	4:56		0.074	0.140							
E-12.....	20	5:15	1580	0.076	0.138	32.32	22.24	32.96	5.38	37.80	6.93	0.13
	22	5:44		0.075	0.165							
	23	6:18	1637	0.074	0.164	33.60	22.58	30.23	4.67	34.44	8.40	0.12
	1	11:20	1612	0.030	0.097	40.07	7.20	36.13	12.43	47.33	5.06	0.26
	3	12:22	1551	0.030	0.082	34.13	5.44	43.44	11.97	54.22	5.86	0.22
	5	1:28	1548	0.030	0.099	30.17	4.98	48.50	13.48	60.67	4.12	0.20
	7	1:50	1586	0.031	0.119	30.01	5.08	47.19	12.81	58.71	5.05	0.19
	9	3:19	1583	0.029	0.163	18.63	3.88	62.26	11.25	72.38	4.38	0.14
	11	3:42		0.029	0.166							

^a Parentheses indicate estimated or uncertain values.

TABLE I.—(Continued)

Heat	Steel Test	Clock Time	Temperature, Deg. C.	In Metal		In Slag						
				S	O	CaO	SiO ₂	FeO	Fe ₂ O ₃	FeO Total	MgO	S
E-12 (Cont.)...	12	4:25	1605	0.028	0.171	15.44	3.52	65.96	10.42	75.34	4.37	0.12
	14	4:52		0.026	0.116							
	15	5:28	(1605)	0.026	0.119	24.57	2.82	56.43	11.14	66.45	4.47	0.15
	17	5:55	1607	0.026	0.133	24.46	2.82	57.23	10.42	66.60	4.27	0.14
	19	6:16		0.045	0.116							
	20	6:39	1590	0.042	0.094	32.48	2.78	47.32	12.82	58.85	3.95	0.38
E-13.....	1	8:01			0.207							
	2	9:35	1577	0.037	0.192	1.54	1.20	87.78	6.73	93.83	3.23	
	4	10:05	1560		0.189	1.71	1.34	87.22	6.88	93.41	3.06	
	6	10:58	1621		0.241	2.02	1.52	86.23	5.94	91.58	4.07	
	8	11:53	1670		0.257	2.50	1.72	82.99	6.26	88.63	6.30	
	10	12:35	1680		0.277	1.46	1.10	87.36	5.47	92.28	4.26	
	12	12:35				1.57	1.04	87.50	5.32	92.29	4.43	
	13	1:50	1678		(0.236)	11.38	1.24	71.86	6.57	77.77	7.87	
	16	3:30	1649	0.026	0.120	27.65	1.42	49.03	15.01	62.53	6.65	
E-15.....	1	10:00		0.028	0.165							
	2	11:52	1652	0.028	0.210	22.24	20.72	39.38	4.84	43.73	10.48	0.05
	4	1:16	1678	0.026	0.197	27.74	17.02	39.34	5.69	44.46	8.24	0.06
	6	2:06	1641	0.027	0.180	28.02	17.32	39.22	6.14	44.74	7.88	0.07
	8	2:43	1625	0.025	0.145	29.98	13.58	41.70	7.79	48.70	5.95	0.09
	10	3:21	1624	0.026	0.164	29.76	13.84	41.99	7.07	48.35	6.04	0.09
	12	4:11	1619	0.021	0.116	35.82	9.94	38.52	9.48	47.05	4.84	0.14
	14	5:01	1601	0.018	0.116	34.90	7.38	41.61	10.84	51.36	4.38	0.14
	16	5:42	1632	0.017	0.095	39.81	6.84	38.34	9.83	47.18	4.34	0.15
	18	6:40	1640	0.014	0.091	39.53	5.72	39.83	10.01	48.83	4.09	0.16
	20	7:09	1637	0.024	0.085	39.25	5.46	39.13	10.79	48.83	4.44	0.25
E-16.....	1	9:58		0.023	0.142							
	2	11:11	1545	0.019	0.133	17.00	2.78	66.34	10.22	75.54	2.74	0.13
	4	11:38	1619	0.020	0.168							
	6	12:12	1636	0.022	0.194	18.63	11.22	56.53	6.69	62.55	6.58	0.07
	8	1:10	1648	0.022	0.238	19.11	14.26	51.73	6.56	57.03	8.18	0.06
	10	2:07	1660	0.022	0.225	16.69	21.22	45.09	4.63	49.26	12.66	0.04
	12	2:40	1632			17.55	21.78	44.23	4.37	48.17	12.22	0.04
	14	3:15	1597	0.024	0.191	14.34	26.02	41.00	3.45	44.10	15.22	0.03
	16	4:02	1616	0.023	0.170	13.15	27.52	38.81	2.76	41.29	17.56	0.03
	18	4:40	1608	0.024	0.173	11.75	29.22	36.62	3.10	39.41	19.20	0.03
	Final Slag					11.54	29.24	35.96	2.79	38.47	19.82	0.03
E-17.....	2	11:52	1617	0.023	0.219	0.37	1.46	87.54	5.92	92.86	4.11	0.09
	4	1:25	1619	0.021	0.241	0.23	1.42	89.50	5.22	94.20	3.06	0.08
	5	2:45	1731	0.019	0.245	0.25	1.48	88.71	4.27	92.55	5.10	0.07
	7	4:00	1757	0.020	0.346	0.33	1.60	88.17	3.66	91.47	5.74	0.08
	9	4:40	1754	0.018	0.290	0.31	1.54	88.40	3.74	91.77	5.87	0.08
	12	5:33	1701	0.019	0.308	0.21	1.68	88.48	4.35	92.40	5.04	0.08
	14	5:56	1657	0.021	0.276							
	17	6:27	1661	0.021	0.262	0.35	1.96	87.85	4.70	92.08	4.72	0.08
E-18.....	1	10:01		0.020	0.297							
	2	11:30	1654	0.022	0.245	<0.2	0.64	90.49	5.74	95.65	3.03	0.09
	4	12:12	1590	0.023	0.216	<0.2	0.72	90.39	5.86	95.67	2.69	0.09
	6	1:30	1625	0.023	0.216	5.71	0.82	82.65	7.02	88.97	3.32	0.09
	8	1:55		0.021	0.204							
	9	2:40	1628		0.210	8.01	1.06	79.66	7.02	85.98	3.78	0.09
	11	4:11	(1620)	0.021	0.240	10.00	1.20	74.72	6.75	80.79	6.10	0.08
	13	4:31		0.025	0.217							
	14	5:06	1617	0.026	0.213	8.46	11.80	65.73	5.74	70.89	7.86	0.06
E-19.....	1	10:31		0.023	0.189							
	2	11:56	1623	0.023	0.240	<0.2	0.92	88.45	6.92	94.68	3.85	0.08
	4	12:59	1649	0.044	0.235	10.91	7.60	67.39	6.78	73.49	6.55	0.13
	6	1:45			0.246	17.72	11.92	53.66	8.39	61.21	7.75	0.11
	8	2:38	1719	0.045	0.249	16.75	11.60	55.46	6.67	61.46	9.40	0.10
	10	3:35	1723	0.044	0.222	16.09	11.66	55.86	5.62	60.92	9.77	0.10
	12	4:04			0.211							
	13	4:35	1624	0.043	0.197	16.87	12.50	55.01	7.28	61.56	7.78	0.10
	15	4:52			0.197							
	16	5:12			0.200							
	17	5:30	1639	0.043	0.205	24.97	16.72	43.72	5.40	48.57	8.24	0.09
	20	5:50			0.202							
	21	6:00			0.243							
	23	6:15	1623	0.045	0.210	25.90	22.80	35.32	4.42	39.30	10.85	0.06
	25	6:28		0.040	0.147							
	26	6:38		0.046	0.154							
	27	6:48		0.046	0.155							
	28	7:17	1608	0.046	0.160	25.32	29.04	26.85	2.88	29.44	15.18	0.04
E-20.....	1	10:05		0.030	0.188							
	2	11:22	1593	0.028	0.229	0.82	1.18	85.72	6.07	91.17	6.20	0.11
	4	12:11	1627	0.030	0.236	9.43	9.76	66.54	6.26	72.18	7.55	0.08

TABLE I.—(Continued)

Heat	Steel Test	Clock Time	Temperature, Deg. C.	In Metal		In Slag						
				S	O	CaO	SiO ₂	FeO	Fe ₂ O ₃	FeO Total	MgO	S
E-20 (Cont.)...	6	12:54	1640	0.049	0.237	15.31	15.80	53.16	5.85	58.43	9.19	0.09
	8	1:45	1657	0.051	0.230	20.72	20.72	43.92	4.92	48.36	9.81	0.08
	10	2:58	1649	0.048	0.219	27.38	26.52	32.62	3.62	35.89	9.27	0.06
	12	3:26		0.049	0.179							
	13	3:52	1643	0.049	0.174	30.26	27.76	25.43	3.10	28.22	13.18	0.05
	15	4:04		0.049	0.163							
	16	4:09		0.049	0.168							
	17	4:26		0.049	0.177							
	18	4:53	1602	0.048	0.163	26.49	23.78	35.02	4.19	38.79	10.32	0.06
	20	5:24		0.047	0.169							
	21	5:50	1638	0.046	0.176	32.49	22.08	30.91	4.84	35.27	9.48	0.08
	23			0.044	0.179							
	24	6:50	1610	0.042	0.172	28.85	18.10	39.21	5.85	44.47	7.57	0.09
E-21.....	1	11:40		0.025	0.198							
	2	1:45	1592	0.026	0.223	<0.1	1.54	86.83	6.73	92.88	3.79	0.09
	4	2:40	1600	0.026	0.231	<0.1	1.74	86.42	6.57	92.33	3.89	0.08
	7	3:52	1617	0.024	0.198	7.22	1.70	79.77	6.90	85.53	3.72	0.08
	9	4:50	1619	0.022	0.179	13.05	1.72	71.34	9.28	79.69	4.00	0.09
	12	5:35	1611	0.020	0.151	17.32	2.08	65.43	10.59	74.98	3.69	0.09
	14	6:25	1630	0.020	0.138	21.11	1.94	60.72	10.71	70.38	4.34	0.09
	16	7:14	1659	0.018	0.159	20.85	2.06	61.23	10.93	71.07	4.64	0.09
	18	7:53	1653	0.019	0.172	20.79	2.10	61.69	9.63	70.37	4.90	0.09
	20	7:55	1680	0.018	0.167							
	E-22.....	1	9:55		0.033	0.162						
2		11:22	1545	0.030	0.189	0.60	0.48	90.50	6.26	96.14	2.44	0.13
4		12:15	1643	0.028	0.264	0.99	0.76	89.32	5.76	94.51	3.86	0.11
6		1:38		0.023	0.206	15.59	0.85	70.25	8.65	78.04	4.45	0.12
8		1:53	1677									
8		3:07	1602	0.023	0.158	15.69	2.02	69.07	9.85	77.94	3.68	0.12
11		3:52	1615	0.022	0.145	21.90	1.36	61.04	11.94	71.78	3.74	0.13
12		4:35	1596	0.020	0.118	26.01	1.44	56.30	12.33	67.41	3.61	0.14
14		5:26	1638	0.021	0.117	35.24	0.94	42.48	9.88	51.38	4.97	0.13
16		6:06	1605	0.023	0.109	41.69	31.40	12.27	1.86	13.94	12.26	0.03
18		6:48	1596	0.026	0.091	37.39	33.08	14.51	0.84	15.27	12.99	0.02
20		7:31	1586	0.026	0.096	31.81	34.86	15.58	0.95	16.43	16.17	0.02
22		8:06	1604	0.026	0.166	23.60	25.40	35.60	3.45	38.71	11.33	0.03
24		8:44	1590	0.025	0.178	17.98	18.68	49.83	5.53	53.81	8.47	0.05
26		9:25	1601	0.025	0.196	14.19	13.94	57.87	6.83	64.02	6.90	0.06
28		9:55	1604	0.026	0.186	16.26	21.66	48.42	4.51	52.48	8.56	0.05
30		10:34	1598	0.027	0.182	12.95	20.40	51.02	4.46	55.04	10.51	0.04
E-24.....	1	10:55			0.213							
	2	12:03	1522		0.186	<0.1	0.60	91.73	5.14	96.43	2.29	0.10
	6	12:34	1700									
E-25.....	6	2:15	1820		0.380	<0.1	0.98	89.22	2.49	91.28	7.15	0.07
	2	12:00	1715		0.300	<0.1	0.54	88.61	4.74	92.87	6.08	0.08
	5	1:00	1560									
E-26 ^b	5	1:35	1582		0.189	<0.1	9.62	76.71	5.63	81.77	7.70	0.06
	9	2:15	1602		0.197	<0.1	15.24	67.58	5.20	72.26	12.42	0.04
	11	2:52	1605		0.193	<0.1	18.76	60.33	5.09	64.91	15.31	0.04
	2	11:29	1720		0.145	tr.	48.32	49.78	1.37	51.00		
E-28.....	4	11:46	1685		0.106	tr.	50.14	48.15	1.25	49.27		
	6	12:08	1625		0.101	tr.	50.18	47.95	1.48	49.27		
	9	12:40	1602		0.087	0.80	48.32	49.18	1.25	50.30		
	12	1:12	1618		0.096	7.20	52.84	38.17	1.43	39.47		
	15	1:53	1627		0.081	11.75	54.34	32.89	1.25	34.00		
	17	2:35	1585		0.056	12.03	52.66	35.09	1.31	36.27		
	19	3:14	1575		0.040	17.02	54.40	28.12	1.31	29.29		
	21	3:29	1590		0.044							
	22	4:01	1608		0.029	20.62	58.68	20.02	0.86	20.79		
	24	4:36	1608		0.021	26.34	61.64	12.19	0.68	12.80		
	26	5:13	1588		0.023	30.20	61.00	8.20	0.57	8.71		
	28	5:47	1592		0.016	30.70	61.86	7.53	0.57	8.04		
	30	6:23	1600		0.017	29.21	63.40	6.87	0.63	7.44		
	1	10:20	1620		0.232	tr.	0.58	89.20	6.27	94.82	3.85	0.08
	3	10:28	(1575)		0.203	tr.	0.36	90.96	6.11	96.46	2.72	
	5	11:04	1572		0.186	tr.	0.50	91.21	5.60	96.25	2.62	
9	12:15	1615		0.220	tr.	0.48	90.81	5.83	96.05	2.92	0.07	
11	1:03	1630		0.238	tr.	0.50	90.40	5.94	95.75	3.53		
13	1:32	1623		0.223	tr.	0.54	90.71	5.21	95.41	3.44		
15	2:08	1600		0.211	tr.	0.68	90.35	6.22	95.95	3.21		
18	2:41	1600		0.215	tr.	0.56	90.50	5.72	95.64	3.17	0.07	
20	4:16	1623		0.148	17.56	66.32	10.01	75.32	5.43	0.07		
23	5:23	(1620)		0.160	17.76	66.08	10.29	76.33	4.08			
25	5:38	(1610)		0.161	17.95	66.64	11.17	76.68	4.11			
	5:58	1595										
	6:32	1597		0.170	17.72	0.94	67.48	9.74	76.24	4.32	0.07	

^b Silica crucible.

The oxygen content of metal in equilibrium with these slags was found to depend upon temperature, the relationship being parallel to that previously reported for the simple iron oxide slags.

The oxygen content of the metal at 1600°C. is shown as a function of slag composition in Fig. 2. The distribution ratio, which is by no means constant, is shown in Fig. 3.

The activity of iron oxide in the slag is shown as a function of its composition in Fig. 4.

At equilibrium, the ferric oxide of the slag is not entirely reduced to FeO. The amount remaining is shown in Fig. 5.

The solubility of magnesia in liquid iron oxide in equilibrium with metal has been determined in the range 1540° to 1800°C. Its solubility in CaO-FeO-SiO₂ slags at 1600° is shown in Fig. 7.

The distribution of sulphur between slag and metal is not greatly affected by temperature. It is very dependent upon slag composition (Fig. 8).

Although detailed analysis of the molecular constitution of the slag lies beyond the scope of this paper, it is pointed out that certain features of the data indicate the existence of stable orthosilicates and monoferrites in the liquid slag.

ACKNOWLEDGMENTS

The authors wish to thank their associates, D. L. Guernsey, S. Marshall and T. B. Winkler, for their valued assistance in conducting the experiments and in analyzing the large number of slag and metal samples. Their thanks are extended to the Open Hearth Committee of the American Institute of Mining and Metallurgical Engineers for a fellowship grant, which enabled them to complete this work.

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DISCUSSION

(H. K. Work presiding)

F. G. NORRIS,* Steubenville, Ohio.—On reading this paper hurriedly the first time to get the gist of what the research deals with, what was attempted and what was accomplished, I immediately saw that it is an outstanding work, carefully conducted, containing a vast amount of fundamental data on relations of interest and importance to everyday steel-making problems. The distribution of oxygen and sulphur between slag and metal, the function of ferric oxide, and an improved means of estimating the activity of iron oxide in slags are all problems that have been discussed in one form or another among open-hearth men for a long time. Even the data on the solubility of MgO and the molecular constitution of slag, though not of such apparent immediate application, are of value, especially in the interpretation of various results. Here, a precise and reliable laboratory method has been applied to problems of practical interest, which I may add parenthetically is done all too rarely. In brief, the project is worthy of the support it has received from the Open Hearth Committee.

I hastened then to read, or rather to study, the paper a second time, to become sufficiently familiar with the details of the calculations so that I could follow the computations of the authors, hoping possibly to apply the same method to slag and metal samples from an open-hearth heat, so as to have a basis for estimating the effect of the difference between laboratory and open-hearth conditions, among the chief causes of which are the presence of carbon, the additional slag constituents and the distance from equilibrium. After several readings I am still hazy on the methods of expressing the results. If I were a little smarter I might understand them or if I were a little dumber I would not even care, but as it is I am merely disappointed in having had my interest aroused and not satisfied.

One point that ultimately will probably be cleared up involves the several references to a "previous" paper, which to my knowledge has

* Wheeling Steel Corporation.

not yet been published. Specifically, I want to ask about the method of arriving at the 1.03 subscript for the slag with 94 per cent FeO and 6 per cent Fe_2O_3 . Calculating the total Fe to FeO gives 99.4. Calculating the total oxygen to FeO gives 102.1, which divided by 99.4 gives 1.02717. Is this the method used?

In referring to the temperature correction, it is stated that a similar equation was found for each slag group. What are these equations and how is the method applied?

In regard to the subscript x in the term FeO_x the only statement I can find is that the value of x depends upon temperature and composition. Is FeO_x something that can be calculated for any slag? What is its value and how found for one of the slags of Table 1?

Should not the symbol FeO in Figs. 1, 2, 3, 5, 7 and 8 carry the subscript 1?

Referring to Fig. 2, in the lower SiO_2 slags (those below the $\text{FeO}(\text{Ca Mg})_2\text{SiO}_4$ join), increase in SiO_2 increases the equilibrium oxygen in the metal. This is the same effect that increase of the SiO_2 in open-hearth slag has on the oxygen. In high-silica slags the FeO is lower, but what is present is more effective in oxidizing the bath.

The slag and metal analysis for sulphur sometimes indicate that the sulphur is either in the slag or in the metal; that is, high-sulphur slag accompanies low-sulphur metal, the inference being that it is the sulphur from the metal that increased the sulphur in the slag. This is pretty much the case for heat E-15 (except the last sample). There was evidently a lime addition between samples 10 and 12 which raised the CaO, lowered the sulphur in the metal and consequently raised the sulphur in the slag. This is the relation that seems to be true in open-hearth slags. For other heats, however, it would appear that high-sulphur slag drives sulphur into the metal. This is the tendency in heats E-10, 11 and 12, in which there was a sulphur addition. Neglecting the influence of other factors, is high sulphur or low sulphur in the slag considered more favorable to low sulphur in the metal?

One indication of Table 1 which the authors modestly refrained from mentioning is the tremendous amount of work represented in gathering these data. On many days the heats were continued well after the normal dinner

hour and in one case the sampling period was 12½ hr., which does not include the melting time. The short heats, particularly with the low-lime slags, probably represent breakouts. The only reason that I have raised so many questions is that I feel such a worthy effort justifies, and in fact demands, not an explanation that might be understood by a few but one that cannot be misunderstood by anyone interested enough to read it.

C. E. SIMS,* Columbus, Ohio.—One can readily agree that the authors have done a fine job in collecting and interpreting the data presented in this paper. Much work still remains to be done, however, and in view of this I wish to make one suggestion.

On page 99 it was observed that, although the slags were in equilibrium with metal, all of them contained Fe_2O_3 . It seems to me that the simplest way to regard a slag is to consider it as a solution of molten salts, which may contain an excess of either acid or basic radicals. Such a solution obeys most of the ordinary chemical laws of oxidation, reduction, double decomposition, and equilibrium. The mineral compounds formed during freezing give an insight to the basic or acid properties of the constituents.

Among these it is apparent that FeO is a basic and Fe_2O_3 an acid radical. Fe_2O_4 can be considered as the compound $\text{FeO} \cdot \text{Fe}_2\text{O}_3$. Furthermore, FeO and Fe_2O_3 are not just materials dissolved in the slag; they are integral parts of the slag. The basicity of a slag is not determined by the ratio of $\text{CaO} + \text{MgO}$ to SiO_2 , but rather by the ratio of all the bases to all the acids.

It is well known that in an iron silicate slag all of the FeO is not available for oxidation and that the addition of lime will increase the oxidizing activity by releasing FeO. Likewise, in a strongly basic slag the oxidizing power is increased by the addition of SiO_2 , which releases Fe_2O_3 .

One should expect, therefore, to find Fe_2O_3 present in these slags. When a slag is in equilibrium with a steel bath, the FeO and Fe_2O_3 apparently are present in a definite ratio, which probably is dependent on the basicity of the slag and the total quantity of iron oxide. The

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reaction



allows adjustment in either direction.

The fact that L_0 is so far from being a constant, as mentioned on page 98, would seem to be evidence of solvation of the iron oxides. The activity of the iron oxides is less than the concentration because they are held in chemical combination. The authors have considered this, no doubt, but I believe it deserves more emphasis than it was given.

J. B. CAINE,* Lockland, Ohio.—The authors have given a very clear picture of the effect of iron oxide in the slag on the distribution ratio, $L_0[\% \text{O}]/(\% \text{FeO})$, with basic slags. At first glance this fact is very disconcerting to students of the acid practice, as a number of investigators have found that in acid slags—that is, slags saturated with silica—the distribution ratio L_0 is independent of the slag composition and dependent only on the temperature. Fortunately, however, the authors have included in Table 1 one heat, E-26, that was made in a silica crucible, and therefore under a slag saturated with silica. The distribution ratios L_0 for this heat are compared in Fig. 14 with the results of Körber and Olsen,⁵ Schenck and Bruggman,⁶ and Caine,⁷ and check within the limits of experimental error. There seems to be no correlation between the CaO content and the distribution ratio in these saturated silica slags, although the CaO content varies from 0 to 30 per cent.

Another interesting point is brought out in heat E-26. If this heat was made by adding CaO to the heat between tests, it would seem that the solubility limit of CaO in SiO_2 -FeO slags is about 30 per cent. This point has never been determined before.

With these two points in mind we can theorize at least regarding the effect of the acid-base ratio in the slag on the distribution ratio L_0 . If the dotted portions of the L_0 curves in Fig. 3 are accepted as approximately correct, it would seem that with a given FeO content the L_0 values decrease as the SiO_2 content in the slag increases.

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⁵ Körber and Olsen: *Mitt. Kaiser Wilhelm Inst. Eisenforschung* (1933) 15; (1935) 17.

⁶ Schenck and Bruggman: *Archiv Eisenhüttenwesen* (1933) 15.

⁷ J. B. Caine: *Steel Foundry Facts* (May 1940) No. 3.

Then the only L_0 line in Fig. 3 that would enter the area of saturated silicate slags would be an extension of the 0.0020 line, extended in the same way as the 0.0025 and 0.0030 lines. This distribution ratio of 0.0020 checks with the average value of 0.0018 given at 1600°C. (2900°F.) in Fig. 14 of this dis-

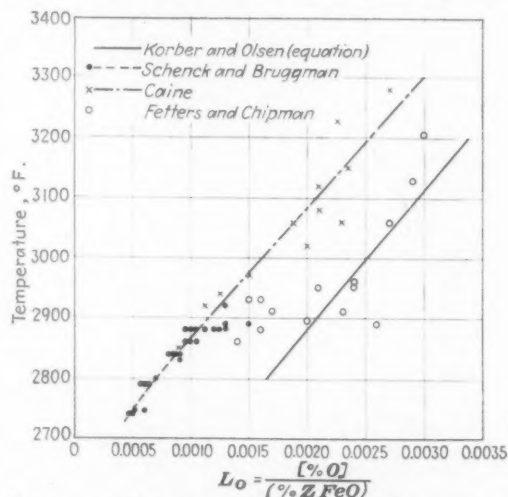


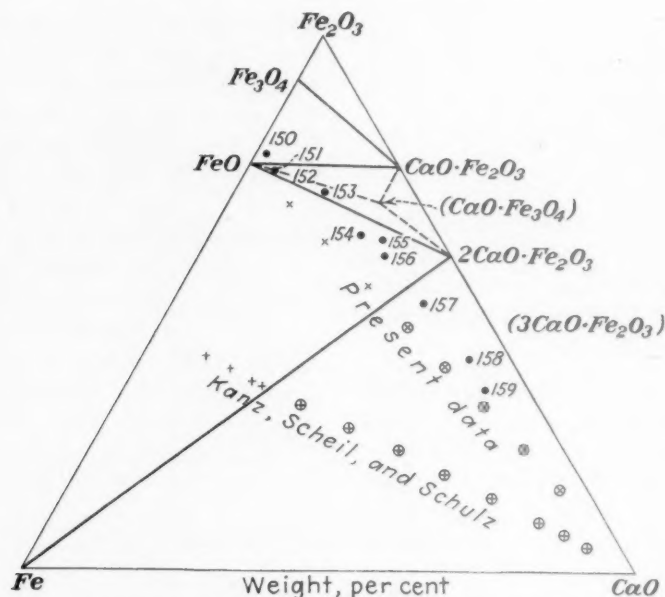
FIG. 12.—DISTRIBUTION RATIO FOR HEAT E-26 COMPARED WITH RESULTS OF OTHER WORKERS.

cussion. All other L_0 lines would fall below this region of saturated silicate slags that is bounded in Fig. 3 by the line joining the 30 per cent saturation limit of CaO in SiO_2 and the 50 per cent saturation limit of FeO in SiO_2 and the SiO_2 corner.

Every once in a while one sees an unsupported statement that acid steels are cleaner than basic steels. If the above theories are valid there may be some support for this statement. As the distribution ratio is so much lower for acid steels than for basic steels, then for a given FeO content in the slag, everything else being equal, there will be a lower FeO content in the metal and fewer inclusions formed by the final deoxidizers.

R. C. GOOD,* Pittsburgh, Pa.—Insofar as steel production also involves additional steps beyond the establishment of equilibrium, or a recognition of the approach being made toward that condition, we believe this type of investigation should be continued. I refer in particular to the tapping operation and the changes that occur at that time. It is

* Metallurgical Engineer, Electro Metallurgical Co.

FIG. 13.—TERNARY SYSTEM $\text{CaO-Fe-Fe}_2\text{O}_3$. (AFTER HAY AND WHITE.)

Present Data:

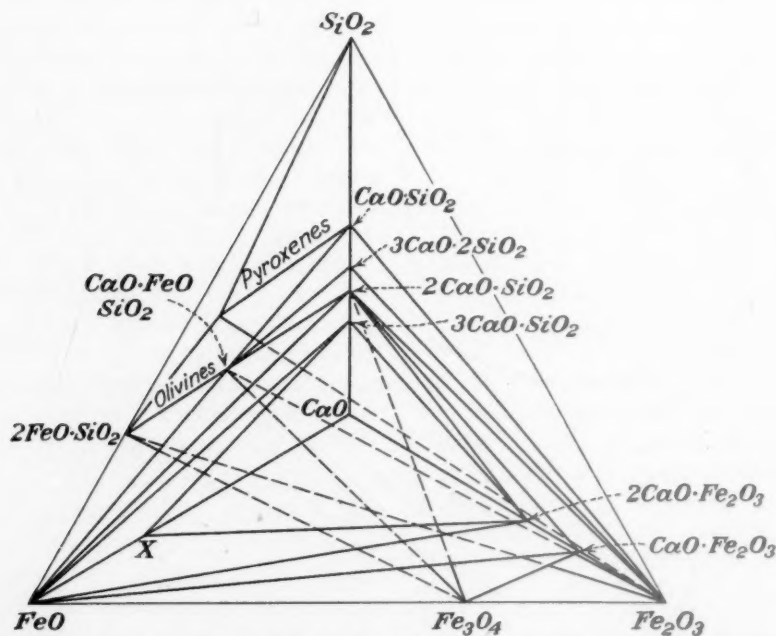
× Melts containing free FeO and calciumferrite (metallic iron also detectable in some).

⊗ Melts containing free CaO and calcium ferrite all of which slaked on standing.

Kanz, Scheil, and Schulz:

× Melts containing iron, $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ and FeO.⊗ Melts containing iron, $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ and CaO.

Crook's melts indicated by • with number of melt along side.

FIG. 14.—QUATERNARY SYSTEM $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ CONSTITUTIONAL RELATIONSHIPS. (AFTER HAY AND WHITE.)

The point X is the intercept of the join $\text{Fe: } 2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ of Fig. 13 with the line joining compositions FeO and CaO.

certainly not an idle thought to suppose that further reactions occur when slag and metal distinctly out of equilibrium are dumped into the same ladle simply because it is convenient. We therefore suggest that if at all possible consideration be given to experiments including this step in the future.

G. SOLER,* Canton, Ohio.—The fairly close agreement of the authors' results with the experimental work of Hay and White⁸ on the system $\text{CaO-Fe-Fe}_2\text{O}_3$ and the system $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ shows that the mineralogical concept of slag study is compatible with chemical equilibria. It is felt that the crystalline constitution of the cooled slag does give an indication of the ionic groupings and forces in the slag that may be represented as Fe^{++} , Fe^{+++} , O^- , Ca^{++} , Mg^{++} , etc. Hay and White show that CaO and FeO are not compatible but that equilibrium exists between $\text{CaO-Fe-2CaO.Fe}_2\text{O}_3$ and $\text{FeO-Fe-2CaO.Fe}_2\text{O}_3$, depending on whether CaO or FeO is present in excess. (See Figs. 13 and 14.)

Hay and White also show in the quaternary representation of the system $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ that mixtures lying in the plane of $2\text{CaO.SiO}_2\text{-FeO-Fe}_2\text{O}_3$ will contain at equilibrium 2CaO:SiO_2 and free iron oxides. If the molecular ratio of CaO to SiO_2 is less than $2:1$, some of the FeO formed during reduction will combine with SiO_2 and will in consequence not be freely reducible. If the ratio is greater than $2:1$ some calcium ferrite will be formed, again decreasing the reducibility. Optimum reducibility is thus found at the $2:1\text{ CaO:SiO}_2$ ratio. This work agrees in general with the conclusions of Fettes and Chipman on the activity of iron oxide in slags shown in Fig. 4 and the effect of basicity on ferric oxide shown in Fig. 5.

K. L. FETTERS AND J. CHIPMAN (authors' reply).—The authors wish to thank those who have contributed to the enlightening discussion, especially Mr. Norris, for his careful reading and well-considered criticisms. His desire to apply new methods of computation to problems of slag behavior in the open hearth is shared by the authors, and indeed is the basis for an

extended research program, part of which is reported in the present paper. Subsequent parts will include the effects of other constituents, especially manganese and phosphorus, upon the several slag-metal equilibria discussed in this paper as well as other reactions that are of interest in steelmaking. Until the behavior of these other constituents has been elucidated, it is not expected that the equilibrium studies will find direct application to the solution of open-hearth problems. These applications probably will involve the use of charts based upon those reported here, but necessarily somewhat more complex, and it is therefore important to remove this haze which seems to obscure the methods of expressing the results.

The symbol x in the formula FeO_x is the ratio of the number of atoms of oxygen to the number of atoms of iron in the two compounds FeO and Fe_2O_3 . It is used for purposes of calculating a mol fraction of iron oxide and is analogous to the use of FeO_t in expressing weight per cent. Mr. Norris' computation is correct. Similar calculations may be applied to any slag analysis which includes both FeO and Fe_2O_3 .

Temperature corrections for oxygen solubility were made by a graphical method, which involved straight lines parallel to the line for liquid iron oxide represented by Eq. 1. The equations for these lines would be of the form: $\log L_0 = -4860/T + B$, where the B term has a characteristic value for each slag group. It seemed simpler to make these corrections ourselves than to overburden the literature with such unimportant equations.

In Figs. 1, 2, 3, 5, 7 and 8 the iron oxide is that found by calculating the total iron of the slag to FeO . Its symbol should have been written FeO_t in all cases. Another error occurs in one of our diagrams. In Fig. 3 the distribution coefficient was defined as $L_0 = [\% \text{O}]/(\% \text{FeO}_t)$ but the value plotted is actually this ratio multiplied by 100.

We have used the ratio $(\% \text{S})/[\% \text{S}]$ at equilibrium as a measure of the desulphurizing power of the slag. This is a much more competent criterion of desulphurizing power than any other simple function and the results are comparable for high-sulphur and for low-sulphur melts. Mr. Norris raises the question: "Neglecting the influence of other factors, is high sulphur

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⁸ *Jnl. West Scotland Iron and Steel Inst.* (1930-40)

or low sulphur in the slag considered more favorable to low sulphur in the metal?" In reply, we would say that other factors cannot be neglected, and that unless some other quantity is specified the question becomes meaningless. The sulphur content of the metal may be regarded as a function of: (1) the total sulphur in the system, metal plus slag; (2) the relative amounts of metal and slag; and (3) the distribution of the sulphur between metal and slag. Relatively larger slag volumes will always favor low sulphur in the metal if (1) and (3) are constant. If (1) and (2) are constant, low sulphur in the metal is favored by a high distribution ratio $(\%S)/[\%S]$. If (2) and (3) are constant, low sulphur is favored by lower total sulphur in the system. Of these three factors the only one directly related to slag composition is the desulphurization ratio $(\%S)/[\%S]$.

Mr. Caine mentions that the distribution ratio L_0 is independent of slag composition in acid slags. This agrees approximately with our findings as indicated in Fig. 3, where it is shown that in general the variation in L_0 is very much less in silica-saturated than in basic slags.

Heat E-26 was carried out with additions of both lime and ferrosilicon in such a way as to follow along the silica-solubility line. The actual limit obtainable by this practice is slightly greater than 30 per cent CaO and less than 10 per cent FeO. Under these circumstances, the silicon content of the metal becomes an important limitation, and for acid slags it would be possible to approach the left-hand margin of our triangular diagrams only in the presence of very high percentages of silicon in the metal.

We have followed the work of Hay and White, which Dr. Soler mentions, with a great deal of interest. This work and other investigations of equilibria among the crystalline phase of solidified slags has been very enlightening. In extrapolating such observations to higher temperatures, it must be remembered that melting is frequently attended by a decrease in the number of phases present, with a corresponding increase in the possible variation of the system. Thus, while it is true that CaO and FeO are incompatible under the conditions mentioned by Dr. Soler, there is no incompatibility in the liquid slag.

The Acid Bessemer Process of 1940

BY H. W. GRAHAM,* MEMBER A.I.M.E.

(Cleveland Meeting, October 1940)

THE young metallurgist of today who thinks casually of the technical literature of the steel industry might conclude that little has been published concerning the Bessemer process. This conclusion is true as relating to the last decade or two, but there is a fairly voluminous Bessemer literature in the period of 1860 to 1910. Since that time, however, an entirely new level of metallurgical knowledge of steelmaking has been reached; and the present paper is simply an effort to look broadly from this new level and to bring the recorded history of the process up to date. It is an effort to appraise the acid Bessemer method of steelmaking in the light of today's technical knowledge thereof.

In this paper matters of history will be dealt with only insofar as they contribute to an understanding of today's situation. Attention will be directed to the apparent causes of past developments in seeking to perceive the true direction of trends now in existence and effective as bearing upon future developments. The paper will discuss the economics of the Bessemer process, but only to the extent that will bear upon the metallurgist's understanding of his responsibility. The problem of the quality of Bessemer steel will be reviewed and examples will be given of the technical data upon which the reasoning of the paper is based. Matters of engineering design, mechanical maintenance, operation and metallurgical investigation will be surveyed. Comparisons will be made between the Bessemer

and open-hearth processes for the sake of clear and ready understanding.

PRODUCTION

First of all it is considered logical and informative to show how much Bessemer steel has been and is being produced, and the relation of that production to the tonnage made by the open-hearth process. Table 1 shows the tonnages made by the two processes in representative years. It is to be noted that these figures are in net tons of 2000 lb., whereas previous to 1940 the Institute figures were compiled in gross tons. Acid open-hearth production and steel going into castings are included, since separated data are not available for the early years of the period covered.

TABLE 1.—*Bessemer and Open-hearth Production*
NET TONS OF 2000 POUNDS

Year	Bessemer, Tons	Open Hearth, Tons	Ratio Bessemer to Open Hearth
1886	2,541,493	245,250	10.36
1890	4,131,536	574,820	7.19
1895	5,498,223	1,273,644	4.32
1900	7,486,942	3,805,911	1.97
1905	12,254,340	10,047,941	1.22
1910	10,542,305	18,485,050	0.57
1915	9,281,679	26,520,594	0.35
1920	9,949,057	36,592,522	0.27
1925	7,530,837	42,598,627	0.18
1929	7,977,210	54,155,235	0.15
1930	5,639,714	39,255,073	0.14
1932	1,715,925	13,336,210	0.13
1935	3,175,235	34,401,280	0.092
1939	3,358,916	48,409,800	0.070

Figures taken from records of the American Iron and Steel Institute, which began with the year of 1886.

The ratio shown in Table 1 is merely the Bessemer tonnage for a given year divided by the open-hearth tonnage of the same

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* Director of Metallurgy and Research, Jones and Laughlin Steel Corporation, Pittsburgh, Pa.

year. In 1886 there were 10 times as much Bessemer steel as open-hearth, but in 1939 there were only 0.07 ton of Bessemer steel produced to every ton of open-hearth steel. This ratio is plotted in Fig. 1. While Fig. 1 seems to indicate that the Bessemer situation is leveling off at a very low figure, when the data for the period of 1920-1929 are replotted on a larger vertical scale the trend still leads steadily downward (Fig. 2).

The ratio shown in Figs. 1 and 2 constitutes a measure of the demand for Bessemer steel in relation to the demand for open-hearth steel. The uniformity of its trend is striking, and the ratio for the next few years can be predicted with precision. Only new applications for Bessemer steel where open-hearth has been used (or entirely new Bessemer products) will change the trend of this line.

A condensed view of Bessemer and open-hearth tonnage is shown in Table 2, giving the production by decades; and the same data are shown graphically in Fig. 3.

TABLE 2.—*Production by Decades*
NET TONS OF 2000 POUNDS

Decade (Inclusive)	Open Hearth	Bessemer	Total
1890-1899	14,008,805	51,958,415	65,967,220
1900-1909	88,829,931	102,279,180	191,109,111
1910-1919	271,387,204	100,720,580	372,107,784
1920-1929	396,826,453	74,810,357	471,636,810
1930-1939	339,460,846	32,261,865	371,722,711

Even though production of Bessemer steel has currently dropped back to about one-fourth of its largest figure in 1906, it is still second by a good margin in steelmaking methods. The still important position of the Bessemer process is further indicated by the very considerable tonnage of blown metal made by the Bessemer converter for the open-hearth duplex method, which is reported as open-hearth production. In this connection the tonnages shown in Table 3 are of interest.

Having viewed figures and diagrams that show a steady movement to open-hearth

production at the expense of Bessemer operation, it will be informative to examine the causes back of this changing relationship.

TABLE 3.—*Production by Processes, 1939*

NET TONS OF 2000 POUNDS	
Open-hearth ingots, basic (including duplex).....	47,788,763
Bessemer ingots.....	3,358,916
Open-hearth ingots, acid.....	437,307
Duplex blown metal (becomes open-hearth ingots).....	2,317,382
Total blown in Bessemer converters.....	5,676,298
Crucible steel.....	931
Electric and all other.....	951,522
Total steel ingots.....	52,537,439

AVAILABILITY OF SCRAP

While even the most casual thinker realizes that the relationship of Bessemer and open-hearth tonnages is influenced by the availability of steel scrap, few realize the extent of the domination of the scrap market upon this relationship, particularly upon the probable future of the Bessemer process.

Initially it would have been difficult for the steel industry to enter rapidly upon a large-tonnage production with any equipment other than a Bessemer converter plant, independent as it is of steel-scrap supply. The Bessemer process uses little scrap, say 5 to 15 per cent of the metallic charge, where the open hearth uses ordinarily some 50 to 60 per cent. The bloom butts, crop ends, and like scrap incidental to steel-works operation is the same for both processes, say perhaps 15 to 20 per cent. The Bessemer process is more than self-sufficient on scrap and produces a scrap as a by-product. The open hearth constantly uses more scrap than it produces and this deficit must be supplied by trade scrap originating from previously manufactured steel articles. Only a very small tonnage of steel, and even wrought iron, was manufactured and consumed in the decade or two previous to 1880 and the volume of trade scrap available for steelmaking was insignificant. The introduction of the Bessemer process was therefore very largely responsible for the rapidity with which the industry could advance. In 1886, for instance, the steel pro-

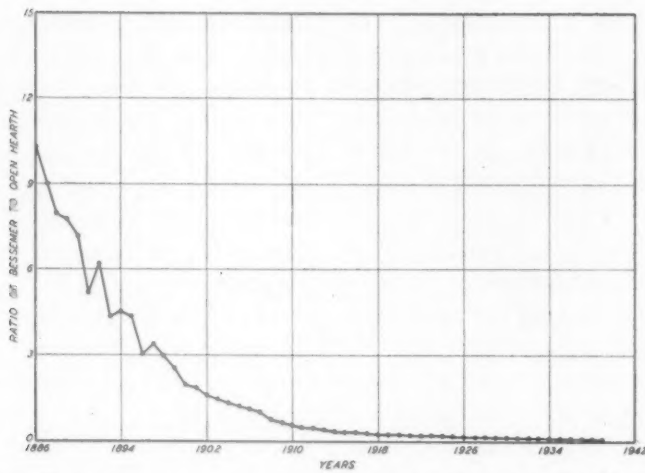


FIG. 1.—RATIO OF BESSEMER STEEL TO OPEN-HEARTH STEEL BY YEARS FROM 1886 TO 1939 INCLUSIVE.

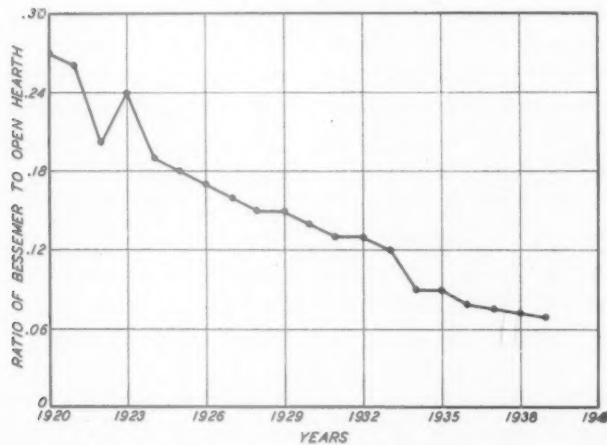


FIG. 2.—END PORTION OF FIG. 1 PLOTTED ON LARGER SCALE FOR LAST TWO DECADES TO SHOW MORE CLEARLY PRESENT TREND.

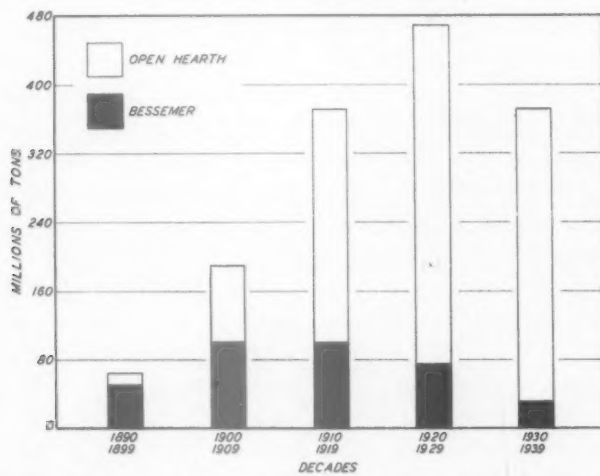


FIG. 3.—TOTAL TONNAGE BY DECADES FOR BESSEMER, OPEN-HEARTH, AND TOTAL PRODUCTION TO 1940.

duction in the United States was 245,250 tons of open-hearth steel and 2,541,493 tons of Bessemer. If it had been necessary to make all of this total production of 2,786,743 tons by the open-hearth process with a 60 per cent scrap charge, the assembly of such an amount of scrap at that stage of the industry's history would have been a difficult, if not impossible problem.

The increase of steel tonnage continued more or less steadily to 1929; and even the Bessemer tonnage increased, or at least held its own, until 1920. With this constantly increasing tonnage more and more scrap was available, to the ultimate disadvantage of the production of Bessemer steel, since such ready availability of scrap obviously favored the open-hearth process.

Aside from the general effect on the scrap situation of continually increasing tonnage, scrap availability has also been favored by other factors, among which were those that tended toward more rapid obsolescence of articles made of steel. It is impossible to very accurately set a figure for the useful life of steel products; but in the early history of the industry much of its product went into railroad, building, and bridge construction, with relatively long life.

Later the upset conditions of the World War created much scrap from steel of very short life. In 1920-1930 came large numbers of automobiles with a useful life of some seven years, and a huge increase in the use of tinplate that became scrap in one to three years. But today, aside from a few scattered applications, one would expect that the average useful life of a piece of steel will not further decrease but may even increase with steady improvement and wider applications of protective coatings.

As long as the total steel tonnage manufactured was increasing, as long as the Bessemer process, with scrap as a by-product well beyond its own small needs, was a large factor in such production, and with the aid of a more rapid obsolescence of fabricated steel products, scrap was bound

to become more and more readily available. But in the past decade these conditions have changed and an increased supply of scrap can no longer be depended upon. The increase of per capita demand for steel has slowed down and any great extension thereof cannot be expected with assurance. Production of Bessemer steel is proportionately so low that its contribution to the supply of scrap is not of great importance. No particular further decrease in the useful life of steel to turn products into scrap in a shorter time can be expected. Therefore it appears that trends in the history of the steel industry favoring an increased availability of scrap have run their course and have become progressively less effective. If correct, these considerations justify earnest attention to an increased use of the Bessemer converter as at least a partial protection against a decreasing availability of scrap.

It is not the intention of this paper to suggest that the justification for the continuance of the Bessemer process rests upon the fact that it produces more scrap than it consumes. It is merely intended to point out that at present levels the production of Bessemer steel is much too low for a correct balance of processes within the steel industry, and that this factor will continue to exert its economic pressure in the direction of increased Bessemer production.

There may be question as to the justification of discussing steel scrap to this length in a technical paper, but technologists are too prone to forget that metallurgy and economics are inextricably intertwined. The real purpose of this discussion of scrap is to show the metallurgist that the economic trends of the next decade or two include elements that will favor a revival of converter operation for Bessemer ingots or duplex metal, and only one factor really limits the extent of that revival. That one limitation is the rapidity and completeness with which management, operators, and metallurgists can solve such manufacturing

and quality problems as are involved. With the present high level of technical knowledge, with improved instrumentation available, and with an economic urge to do the job, there should be rapid progress.

INVESTMENT COSTS

Aside from the availability of scrap, a further economic factor exerted its influence in that, once the steel industry had reached a reasonably established state, investment costs began to apply a considerable influence on the proportion of steel made by the Bessemer and open-hearth processes. Toward and even after the turn of the century, the rapidly growing industrialism of the United States demanded increased steel-making capacity. Financiers naturally were attracted by the fact that, since scrap had become a widely available and usually rather cheap article of commerce, an open-hearth plant using 60 per cent scrap could be built with only 40 per cent of the investment for blast furnaces as compared to the cost of ironmaking facilities for a Bessemer plant using practically 100 per cent pig iron. This fact undoubtedly played a part in the rapidly shifting balance of open-hearth steel most noticeable in the period of 1900 to 1910.

PRODUCT LOSSES

Aside from economic factors operating against the Bessemer process, the method sustained serious losses in its products between 1900 and 1940 for a combination of metallurgical and mechanical reasons.

From the standpoint of product application, the Bessemer process first lost rails because of a poor reputation for dependability; and on much the same count it not long thereafter ceased to be used for heavy structural sections. The large-scale development of seamless pipe that occurred in the period of 1910 to 1930 went almost entirely into the open-hearth bracket, doing little to actually decrease the Bessemer tonnage but still greatly swelling the balance in favor of

the open-hearth process. Almost the same statement, with the same result, can be made concerning the expansion of the manufacture of flat-rolled steel from 1920 to 1940; but the development of the continuous strip mill did greatly decrease Bessemer tonnage in that it took over tinplate, which had included much Bessemer on the old hot mills. The steel plants that developed the continuous strip mill had, it so happened, little or no Bessemer capacity and were not interested in developing its application to the continuous rolling method. Latterly some Bessemer is being cold-rolled into tinplate but the matter moves slowly.

This discussion leads finally to consideration of the more purely metallurgical phases of the Bessemer situation of today as it emerges from the past.

METALLURGICAL HISTORY

There are easily detectable characteristics about any industrial method that grew up without the benefit of technical help, and these appearances are very marked about the Bessemer process. Almost up to the present day, Bessemer operations proceeded with no benefit of technical supervision and assistance. A generation ago the Bessemer blower's responsibility to his superior rested more in his ability to keep out of trouble than it did in turning out a high quality of product, and keeping out of trouble meant particularly the avoidance of cold heats and heavily skulled ladles. Because of the blower's constant "playing safe" on temperature, heats were usually on the high side in temperature and frequently excessively so. This contributed to pipe, porosity, laminations, segregation, and to increased nitrogen content, materially favoring greater sensitivity to aging and embrittlement by cold-work, all of which meant increased likelihood of breakage in fabrication and in service.

Of course there was in those years a kind of embryonic appreciation of the effects of

varying degrees of oxidation and the blower did blow "young" or "full" for an elementary and rather clumsy kind of control, but in competition with open-hearth steel, Bessemer steel in the period from 1900 to 1910 had little chance of a favorable or even comparable showing. With no metallurgical staff in existence, with manufacturing organizations that almost wholly failed to understand the technical points involved, and with a consuming trade so uninformed as to say "it breaks because it is high in phosphorus," it is a wonder only that Bessemer steel continued as long and in as large volume as it did.

It is a fact that throughout its history Bessemer steel has had certain qualities which in selected applications made it preferable, but a generation ago those qualities were not well understood and it was often applied where unsuited. The problem facing the Bessemer-steel metallurgist today is not just to change the inherent qualities of Bessemer steel but rather to identify them and derive control of these characteristics so that they can be reproducibly placed at will at any given desired value.

In the past several decades Bessemer steelmaking has been neglected alike by management, sales, operators and technologists. It would be hard to find any phase of the steel industry a more fruitful field for research than the Bessemer process of today, or any field wherein results obtained would contribute to larger or more important economic and commercial considerations. Many steel companies have had large investments in Bessemer facilities; and these producers, faced by seriously diminishing use for these facilities, have been writing off their investment, abandoning it without a struggle. Strangely enough, it is the technologist that is raising a question about the wisdom and necessity for this course. He has suggested to the manager that if the Bessemer process were given even a portion of the lavish technical aid provided for the open-hearth process, it

might regain its proportionate place, retaining its undoubted inherent advantages. An examination of this suggested position will be enlightening, even if the case is not proved.

INHERENT FACTORS

In the past the charge has been made with some justice that Bessemer steel was less uniform than the open-hearth product. From a manufacturing point of view, the Bessemer process has certain elements of variability that contribute to nonuniformity and render control and metallurgical supervision difficult, partly through lack of chemical and physical control of the Bessemer process and partly because of the specific fact that Bessemer blows have been of smaller tonnage than open-hearth melts. Today 150 tons of open-hearth steel would be made in a furnace at one time, representing a single set of values by any system of judging and evaluation. But even in the largest acid converters of today it would require six blows to make 150 tons of Bessemer steel, and that means six different sets of physical properties and six varying levels of workability and service qualities. This must be a disadvantage unless, as we now begin to see may be possible, the Bessemer process may perhaps be controlled with a precision that will be impossible in open-hearth steelmaking.

In speed of operation the Bessemer method proceeds so rapidly that variations in timing are serious in their effect on the product. The open-hearth melter deals with a finishing period of 1 to 2 hr. and variations in tapping time may extend to perhaps 15 min. without serious results, but the Bessemer blower is concerned with a finishing period of not more than one minute and his tapping times must be correct by a matter of seconds. This condition, too, might be considered as an insurmountably serious disadvantage of the process, but it will not be so if control measures of a comparable rapidity in time can be developed.

BASIS FOR CONTROL

There is about the Bessemer process a simplicity that under sufficiently well organized handling should do much to support it in competition with other methods of steelmaking. In its essentials, the process involves only one raw material—liquid pig iron, to which only one material is added during processing—compressed air. The finishing operation consists of the simple movement of a lever to turn down the vessel. The process is in a considerable sense automatic.

Two blows of Bessemer steel will be alike if blown from iron of the same analysis and "turned down" at precisely the same point. This may be stated a little differently by saying that two blows will be alike if blown at the same temperature and turned down at the same point. Variations in the heat-producing constituents of the iron may be compensated for by variation in the cooling materials used. The usual cooling materials are steam, scrap or iron ore, all of which in one way or another absorb heat from the liquid bath. Iron ore also increases the slag volume and by assisting to oxidize the silicon shortens the blowing time as much as 20 to 30 per cent. Bessemer operators and metallurgists have long been suspicious of steam as a coolant, supposedly because of the absorption of hydrogen. There is considerable difficulty, however, in isolating the effect of steam from other variables, and the case against it is certainly not clearly established. If no other alternative were available it would seem better to use steam than to allow a blow to progress and finish at too high a temperature.

While it is possible, in theory at least, to control the quantity of coolants used, based upon the silicon content of the iron, there are practical difficulties in the way of originating dependable tables showing weights of scrap or ore to be added or steam to be used. A fair share of troubles with the quality of Bessemer steel are far from being

purely the responsibility of the Bessemer operator. Many of these troubles trace to a combination of variations in iron quality with the peculiar operating characteristics of the Bessemer converter. The Bessemer blower has to deal with iron that may vary rather widely from charge to charge in heat-producing constituents, nor does he know with any degree of accuracy what this variation is. Under such circumstances his control of temperature can only be all too uncertain.

Iron analysis available in a steel plant is ordinarily the average for an entire blast-furnace "cast" of perhaps 150 tons, and the range of silicon content between maximum and minimum covered by the average reported for a cast may be considerable. There is always a good bit of uncertainty as to the degree of mixing that actually takes place in a mixer, and the mixer operator is never too certain as to the proportionate weight of partly used casts of iron still remaining in the mixer. The usual calculated "mixer analysis" as provided to the Bessemer operator is very often fairly wide of the mark.

An honest evaluation of the situation leads to the conclusion that until the blower is accurately informed as to the silicon content of the iron being charged into the converter he cannot very fairly be held responsible for considerable variation of temperature. It may be claimed that the blower should be a sufficiently good estimator of temperature to judge the progress of the blow, but it is a little severe to hold the blower as almost the only man in the whole steelworks without instrumental assistance in judging temperature. In any event he can form little estimate until the silicon blow is over, and a really sound estimate of temperature is scarcely possible until the heat is well into the carbon blow.

Quality and uniformity of product is not served by a policy of holding the blower responsible for blowing iron of a (to him) unknown degree of variation in heat-pro-

ducing analysis with no remedial measures possible except additions of coolants, which can be added only after some of the damage of a high temperature has already occurred.

Accepting the problem merely as one of providing the blower with accurate knowledge of the silicon content of the iron he is blowing, it resolves itself into a matter of determining the analysis of the iron drawn from the mixer for a particular blow and of reporting that analysis to the blower when that same iron is being charged into the converter or very quickly thereafter—at least before the temperature of the blow has “gotten out of hand” and while there still remains time to take corrective measures. Analytical technique of this order of speed is not in existence today. Even the most rapid existing spectrochemical procedure would not do much better than report to the blower on the blow previous to the one actually in the vessel. Nevertheless, it does not seem impossible that some method can be developed, and the question is being studied.

The discussion above deals only with determining the extent of such variations as exist in silicon or other heat-producing elements without respect to the control or elimination of such variations. No survey of Bessemer operation can be complete, however, without consideration of these variations. Superficial thinking would be inclined to consider two blows of the same finished quality even if one were made with a higher silicon iron, providing this higher silicon were balanced by a scrap addition to produce the same blowing temperature. Research indicates, however, that variations in silicon affect the quality of finished steel even if temperatures are closely the same. These indications point to the conclusion that for best uniformity of product successive blows should be produced with closely the same slag volume of substantially uniform analysis. Such a situation could presumably be met by operating the blast furnace at a somewhat lower silicon level,

determining the analysis of each charge of iron for the Bessemer, and by addition of ferrosilicon to bring the silicon content *up* to some substantially uniform level.

It is obvious, however, that if this situation assumes the importance suggested here, sensible handling thereof would bring back to the blast-furnace operator an increased measure of responsibility for decreasing the variations in his product. There are methods known for improvements along this line, detailed discussion of which lies beyond the scope of this paper. Realization of these improvements has been retarded by considerations of cost of investment and operation but if the development of methods in the Bessemer to help the blower become seriously expensive, this fact will help to establish a case for improvement in iron uniformity by efforts in the blast-furnace department.

Another feature of the control of temperature in blowing is that the sensible heat of the iron is more important than might be supposed. The development of a dependable device for measuring iron temperatures is highly important and fortunately real progress is being made in this direction. Other considerations also suggest the probable desirability of refrigerating the Bessemer blast to a substantially uniform year-around temperature and moisture content.

— Early in organized research work on Bessemer operation it will be discovered that complete and dependable control of blast pressure and volume is highly desirable. Tabulated records will show that there is an optimum pressure that must be held within fairly close limits. Variations such as may be caused by two converters being blown from a common blast main will rob blower and metallurgist of much of their power of control.

All of this discussion summarizes itself into the statement that in spite of the tremendous simplicity of the Bessemer process with only two raw materials, iron

and air, the quantity and quality of these must be known and controlled to permit control of the quality of the product and uniform reproducibility thereof. The tem-

photocell and amplifier arrangement and a continuous graphic record is obtained of the energy registered. The chart record for a representative blow is shown in Fig. 4.

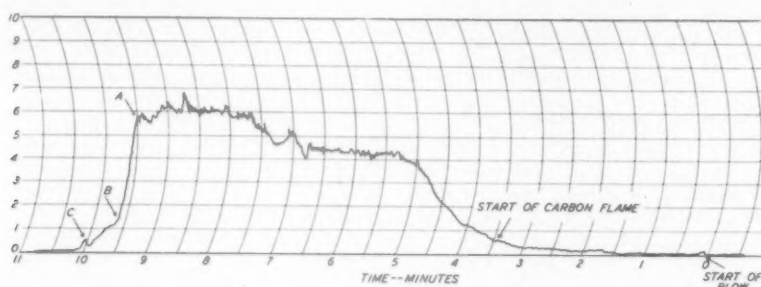


FIG. 4.—A RECORD OF THE LUMINOUS ENERGY OF A REPRESENTATIVE BESSEMER BLOW.

perature of the iron and its heat-producing content must be known and controlled, and the volume of air and its humidity and temperature must be considered. Real progress in Bessemer operation will require much finer manipulation of these factors than has existed in the past. Improvement in this direction will tend to remove the necessity for some of the rather blind and awkward procedure the blower has had to use in the past.

END-POINT DETERMINATION

Since the Bessemer process is essentially automatic in character, it will, if properly charged, proceed satisfactorily; but the end is not automatic. In fact, at a given moment the charge begins to "commit suicide," so to speak, by burning itself back into iron oxide. This change takes place with great rapidity and therefore precise control of the end point becomes a matter of greatest importance.

A few years ago, in the midst of organizing forces for comprehensive and intensive research on the Bessemer process, it was proposed that the luminous energy of the flame as measured by a photocell arrangement might form a basis for control. Subsequent development work by the research and plant metallurgical staffs has produced a method that has very helpful control features. The flame is viewed by a suitable

The chart record in Fig. 4 reads from right to left instead of the usual left to right fashion. The energy of the flame is low during the oxidation of the silicon but increases to a high level during the oxidation of carbon. When the carbon is reduced to about 0.15 per cent, at point A on the chart in Fig. 4, the flame intensity drops quickly to point B, where at about 0.04 per cent carbon there occurs a slight retardation in the rate of decrease of flame energy. The change at point B is a critical moment in the end of the Bessemer blow and B is an important datum point on the "electric eye" charts. As the vessel is turned downward into a horizontal position, it reaches a point where the steel bath drops below the bottom tuyeres and the unimpeded flame impinges on the shield in front of the converter, producing a "flashback," which registers on the chart at point C. At this point all normal blowing action ceases. The portion of the blow between points B and C is in this paper referred to as the "afterblow," the time in seconds being measured laterally on the chart. The term "afterblow," however, should not be confused with the dephosphorizing afterblow in basic Bessemer practice, since this phase is entirely absent in the operation of acid converters.

The blow in Fig. 4 lasted for 10 min. with an afterblow of 23 sec. The shape of the curve of flame energy is representative but

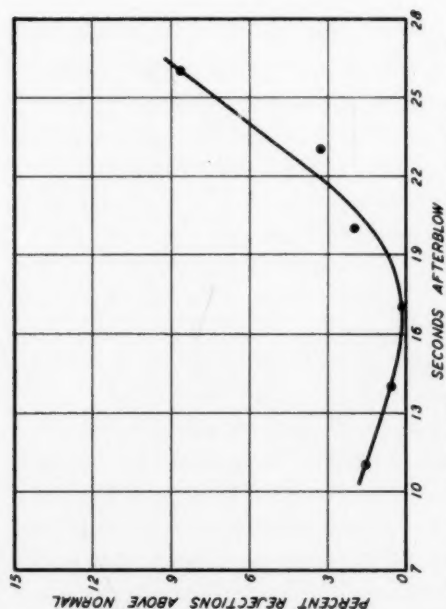


FIG. 5.—EFFECT OF VARIATIONS IN LENGTH OF AFTER-BLOW ON INTERNAL SOUNDNESS OF BESSEMER INGOT AS INDICATED BY CROSS-SECTIONAL ETCH TESTS.

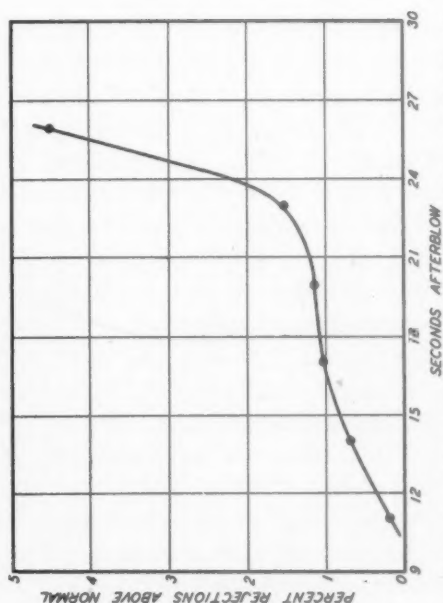


FIG. 6.—RELATIONSHIP OF SURFACE DEFECTS TO LENGTH OF AFTERBLOW AND INDICATION THAT THE OPTIMUM POINT HAS BEEN MISSED BY TOO LONG AFTERBLOWING.

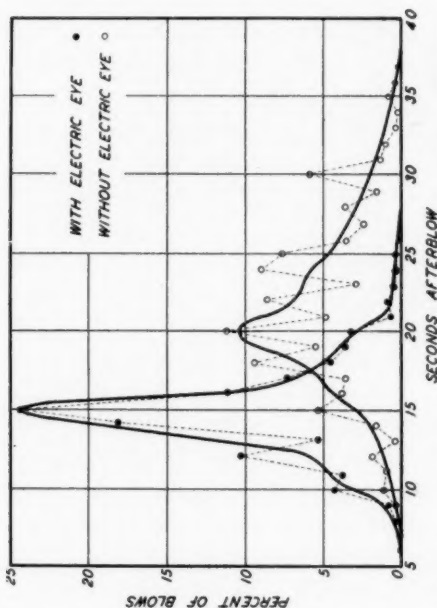


FIG. 7.—FREQUENCY DIAGRAMS FOR THREE MONTHS OPERATION WITHOUT ELECTRIC EYE AND THREE MONTHS WITH IT.

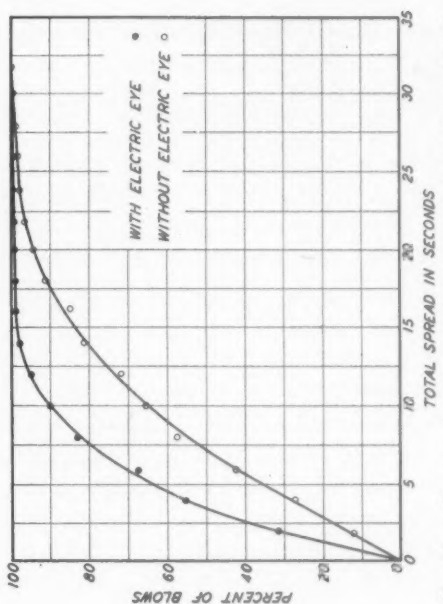


FIG. 8.—QUANTITATIVE FREQUENCY DIAGRAM REPEATING DATA GIVEN IN FIG. 7.

the length of the blow is shorter by 1 or 2 min. than average and the afterblow is 5 to 10 sec. longer than usual.

With this system in operation, it was possible, for the first time in Bessemer history, to check the blower's visual estimations against an instantaneous instrumentally obtained record. It follows that it was for the first time possible to get, devoid of human equation, an evaluation of the time factor at the end of the blow. How fast were reactions proceeding during the critical period? If, for example, iron oxide content of slag and metal were to be kept within certain limits, what did those limits mean with respect to seconds elapsed from the instrumentally recorded end point? No one had ever known whether a difference—call it error or variation, as one will—of 5 sec. was serious or whether 10 sec. or even more was permissible.

Fig. 5 indicates that this situation can be clearly evaluated. Taking point *B* in Fig. 4 as a datum point, Fig. 5 shows how varying the end of the blow affects etch-test rejections of Bessemer screw steel. The study includes results on 13,350 billets, 4 by 4 in. and larger. The curve shows that steel outside of a range of ± 3 sec. from the optimum point increases rapidly in pipe and porosity with corresponding decrease in yield of good material.

It is reasonable that there might be a different optimum point for each grade of steel, or for each standard for quality evaluation, and there is some evidence that this is true. A study such as is diagrammatically shown in Fig. 5 may even show that for a given condition in a given grade of product, the optimum time of turndown is missed entirely. Such a situation is shown in Fig. 6, which plots the percentage of surface defects above normal against the seconds afterblow for approximately 9000 tons of sheet bar. With a precise instrumentally determined end point available, compilation of data such as are shown in

Fig. 6 is simple, and the correction is relatively easy.

Efforts are now being directed to full exploration of the exact length of afterblow that is most favorable for each grade of product and each phase thereof. Where various quality factors in a single grade call for different periods of afterblow, the best possible compromise will be selected. In this way progress may be achieved toward a degree of uniformity never before reached in Bessemer operation.

With the instruments installed for determination of the end point, months were spent in checking the blower's determination. Then gradual advantage was taken of the instrumental determination until finally blowing was based upon the instruments, very little being left to the judgment of the blower. To show the results before and after the time when dependence was first placed on the "electric eye," Figs. 7 and 8 have been prepared. Fig. 7 is a conventional frequency diagram, one line of which shows the performance of blowers based on their own judgment of the flame reactions. The period involved covers three months with a total of 943 blows observed.

One year later the instruments were being depended upon to determine the end point, and the frequency diagram for a second three-months period is also shown in Fig. 7, covering 2781 blows observed. It is evident that the instrumental determination of the end point is yielding a much more uniform performance. The shift of the "electric eye" data to the left is caused merely by the fact that the specified afterblow has deliberately been made somewhat shorter.

Since conventional frequency diagrams are qualitative in character, the data of Fig. 7 are presented in quantitative fashion in Fig. 8 by taking the median point of each of the two groups of data as a zero point and constructing cumulative diagrams therefrom. The time element of Fig. 8

is to be construed as a plus and minus quantity; that is, 5 sec. on the diagram covers a spread of time of $\pm 2\frac{1}{2}$ sec. or a total interval of 5 sec. Fig. 8 indicates, for example, that within a total spread of 5 sec. the installation of the photocell equipment improved the uniformity of the performance from 35 to 64 per cent. In the second three-months period 90 per cent of the blows were within a total spread of 10 seconds.

It would unduly extend the length of this paper to attempt to give any appreciable part of the data already available as to the effect of this improved uniformity on manufacturing and metallurgical conditions. Briefly, it contributes to a narrower range of oxidation conditions, fewer off-heats, savings in ferromanganese, sounder interior of ingots, smaller surface defects, better yields, and narrower ranges of physical properties and workability.

TEMPERATURE CONTROL

The importance of temperature has been referred to previously in this paper, but it should be said here that somewhat better performance has latterly been experienced, which has in part depended upon the photocell equipment. Although this equipment is primarily intended for end-point determination, it can be used to assist in temperature control. Much effort is being directed to closer temperature control but publication of specific data must wait until changes now being made in pyrometric equipment and methods have been more completely developed.

DESIGN AND MAINTENANCE

The struggle for advancement in Bessemer steelmaking to the end of generally improved quality and a high degree of uniform reproducibility involves many details of a more or less mechanical character. This is exemplified by variations in the length of time required from the moment the turn-

down mechanism is set in motion to the moment when all tuyeres are clear of the bath. The blower may, with or without instrument assistance, accurately gauge the status of the flame, but many factors may influence the interval required to clear the tuyeres. Power-supply pressure, either electric or hydraulic, may vary appreciably from moment to moment owing to fluctuating demands from other equipment supplied by the same system. Vessel linings erode and wear away, "kidneys" and vessel skulls build up or burn away, thus increasing or decreasing the speed of rotation of the vessel.

A study of variation in the turndown interval, involving some hundreds of blows, was made on two vessels, one operated electrically and the other hydraulically. A short series of successive blows was selected from this study to show in Fig. 9, which indicates variations that may well be unfavorable to quality and uniformity if the operating crew are not alert to compensate for changes in the rate of vessel rotation. Obviously, new converter installations should be designed, and existing plants altered, to provide very liberally powered rotating mechanism, fed by a power supply as separate as may be possible from other equipment that might produce fluctuations in pressure or voltage.

Fig. 9 makes clear that even if a given blow is turned correctly with reference to point *B* in Fig. 4 it may still be blown some seconds more or less than it should have been, if the blower has improperly gauged the rate of speed of rotation of the vessel. Other parts of this paper, for instance, Fig. 5, show that a variation of this order might unfavorably affect the quality of the product.

Gradual erosion of the lining or slow building up of vessel skulls will produce gradual changes, which can be compensated for by an alert blower, but he can hardly be held responsible for sudden fluctuations in power supply such as inevitably will occur

if other heavy equipment is fed from electric or hydraulic lines used to rotate the converter.

This situation has been discussed at some length because it illustrates one of many

metallurgist in continued study of those phases not yet entirely understood.

This is a very simple policy and one that has been in effect in the open-hearth plant for some years but that as yet is not repre-

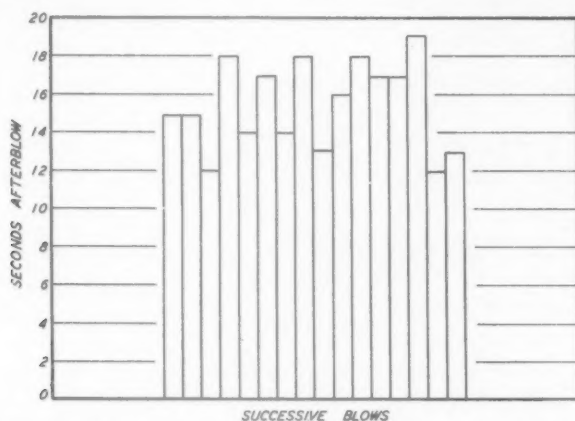


FIG. 9.—VARIATIONS IN LENGTH OF AFTERBLOW DUE TO MECHANICAL CAUSES.

more or less similar reasons for the diminishing position of Bessemer steel. In a distant customer's plant a complaint is registered on a shipment of Bessemer steel, and customer, salesman, and manager take the incident as one more count against Bessemer steel and the Bessemer blower—whereas the cause may really be hydraulic lines of too small a diameter, a detail certainly not chargeable against the process but rather the responsibility of plant management and plant engineer.

If the Bessemer process is to return to its proper place in the steelmaking industry, different thinking and a different attitude will be needed on the part of all concerned—manager, engineer, and operator alike. It is not hard to see what this changed attitude will have to be. There are few real mysteries or obscurities in the picture. The attitude required is merely this: The Bessemer process can be restored to its position if those involved will commit themselves to the improvement of control and to the reduction of causes of variation—to the extent that represents good practice in maintenance and operation of equipment in general, and if they will further support the

sented in Bessemer operation. An example of this situation is to be found in the air-blast supply for a Bessemer converter. True, there remains to be done considerable study of the relation of blast supply to the various features of the Bessemer process; but reasonable control and even investigation is made difficult, if not impossible, in installations where two or more converters are blown from a common main, and in which blast leakage that is serious in volume and varying in degree is tolerated around the converter bottom. The steel-maker would not drive his own auto with gasoline dribbling from a leaky carburetor. He would get it repaired or install a modern and well-designed unit. If he will apply the simple policy of good equipment, well maintained, the Bessemer process can be revived. If he will not do so, the Bessemer process will follow its steady movement toward extinction.

But if this policy is simple and clear, its complete application may be neither easy nor inexpensive. It may require costly re-vamping of blowing equipment, periodical refacing of converter bottoms, and attention to a host of other details.

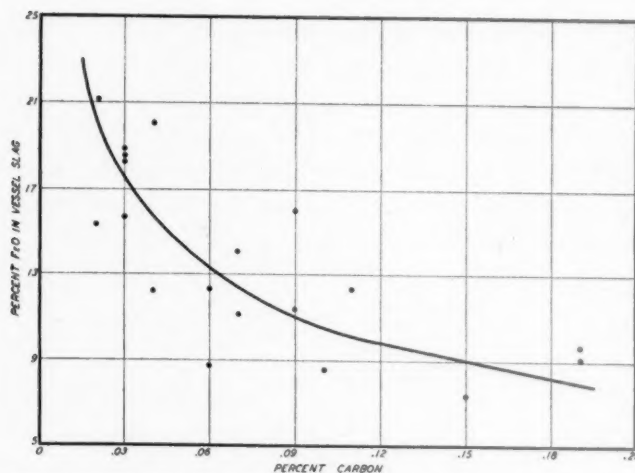


FIG. 10.—EFFECT OF VARYING RELATIONSHIP OF CARBON CONTENT TO IRON OXIDE CONTENT OF VESSEL SLAG.

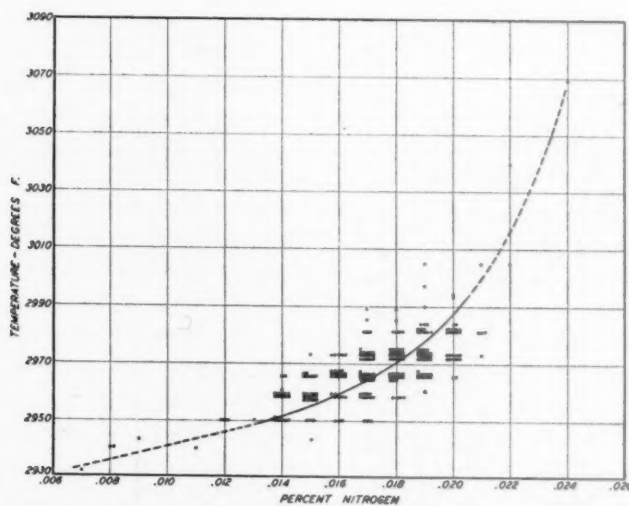


FIG. 11.—NITROGEN AND TEMPERATURE RELATION OF FINISHED BLOW.

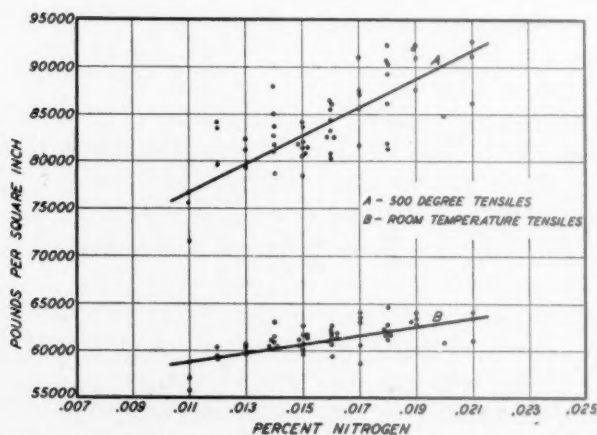


FIG. 12.—NORMAL AND THERMALLY AGED TENSILE STRENGTH IN RELATIONSHIP TO NITROGEN CONTENT.

OXYGEN CONTROL

In dealing with oxygen, the tendency of the Bessemer process to be "automatic" is of appreciable assistance to the operator and to the metallurgist. Granted substantially uniform iron and air blast, control of temperature will not be too difficult and the slag will be reasonably uniform in volume and analysis. To the extent that such conditions prevail, the degree of oxidation will depend entirely upon the time at which the blow is turned down. There is therefore control of degree of oxidation to the extent that there is control of the end point. Fig. 7 shows that instrumental determination of the end point is of great assistance in narrowing variations in the length of the afterblow and therefore contributes to control of the degree of oxidation. In regard to individual blows, however, there are in practical operation conditions of variation that make it improper to conclude that all blows should be of some exact and uniform length of afterblow.

The length of afterblow proportionate to a given degree of oxidation, as necessary in arriving at a uniform manganese efficiency, is affected by weight of iron charged, silicon and manganese content of the iron, and temperature of the blow; but the facts concerning these influences are not yet fully developed and in any event a full discussion of them is beyond the scope of this paper.

Obviously, too, the rate of oxidation reactions will be influenced by the rate at which oxygen is supplied. Since it is common practice to block off or "blank" such tuyeres as become badly eroded during the life of a converter bottom, the number of open tuyeres is gradually decreased and, for any given pressure, oxygen is supplied at a progressively slower rate as more and more tuyeres are blanked, requiring a proportionate increase in the length of the afterblow.

It is assumed that adequate control exists to maintain a constant blast pressure. And, as previously pointed out, attention must be paid to any condition that affects the rate of rotation of the converter from an upright position to the position where the tuyeres are clear of the bath and oxidizing action is stopped.

The foregoing discussion may suggest a somewhat more complex and difficult situation than actually exists. If for the best results on any given quality phase of a given grade of steel the optimum length of afterblow is found to average, say, 16 sec., corrections for factors of variability will not usually change this length of afterblow outside of a range of 14 to 22 seconds.

Because of the broad scope of the present paper, it would not be practicable to give complete data to support each statement or conclusion that is made. Perhaps in later publications individual phases of these Bessemer problems may be more fully discussed with complete and appropriate data. In presenting the broad conception that this paper is intended to set forth, endeavor is made to accompany each phase with an example of the investigational data upon which thinking has been based.

In accordance with this procedure it appears appropriate to show data as to the effect of varying relationship of carbon content at the end of the blow to the iron oxide content of the vessel slag, as in Fig. 10, which is considered to be self-explanatory. In the Bessemer process oxidation conditions are really quite precise, and the degree of scatter in the points of Fig. 10 is present because the data have not been corrected for the effect of known variables. Presumably if the iron oxide in the steel were determined accurately, there would result a very smooth curve for the carbon-iron oxide relationship. By inference, Fig. 10 shows the increase of iron oxide in the slag for increased length of afterblow, since the carbon content decreases as the afterblow progresses.

NITROGEN CONTROL

One of the characteristic features of Bessemer steel is its rather high nitrogen content. Beginning with a pig iron containing from 0.002 to 0.006 per cent nitrogen, finished Bessemer steel ordinarily will contain from 0.011 to 0.020 per cent nitrogen with scattered blows outside of these limits. This fact has been known for years, but the physical chemistry of nitrogen in Bessemer steel has not been adequately explored and the factors governing the form and amount of its occurrence are even now not well understood.

Support can be obtained for the idea that nitrogen solubility is inversely proportional to the carbon content, increasing as the carbon is eliminated from the bath. The data available do generally support this conclusion, but the situation is beclouded by the fact that the temperature increases as the carbon decreases. Superficially, too, one might think of nitrogen increasing with longer blowing time, but this neglects all thought of saturation limitations. It is generally true that longer blowing time usually means higher nitrogen, but it also usually means higher finishing temperatures, since the longer blowing time is largely caused by increased silicon content with consequent higher temperatures because of the greater amount of the heat-producing element present.

At the present writing, it is difficult to make a simple unqualified statement that could stand unchallenged as being theoretically correct in presenting the conditions governing the nitrogen content of Bessemer steel; but chemical composition in general, and particularly carbon content, is generally fixed by the physical properties and workability desired and is not subject to change merely to produce a higher or lower nitrogen.

A tremendous weight of data is available to show that higher nitrogen contents accompany increased temperatures, and for

practical purposes it is dependably sufficient to say that nitrogen can be controlled to a considerable extent by control of temperature.

The relationship of nitrogen content to the temperature of the finished blow is apparently so definite as to make this feature outstanding, as shown in Fig. 11. These data were based upon optical pyrometer measurement of temperature and the scatter of the points may more likely be due to incorrect temperature measurements than to any true deviation from the nitrogen-temperature relationship. In fact, if a given Bessemer blow is high in nitrogen, the metallurgist may with little error assume that it was a hot blow even if he has no temperature data.

For practical purposes, therefore, it is adequate to consider that nitrogen is directly proportional to temperature. One is inclined to speculate a little as to whether the increased nitrogen taken up as the temperature rises is purely a matter of solubility of nitrogen in molten iron, or whether there is present some chemical effect. There would be a certain plausibility to the hypothesis that higher temperature favors the formation of certain nitrides that may form only partially or not at all at lower temperatures. Unfortunately, there is as yet available no real information as to the forms of occurrence of nitrogen in steel, a subject that some day may be found to be of the utmost importance.

In actual operation, by controlling the blow as much as possible toward the cold side, Bessemer steel can be made with nitrogen considerably below the normally expected content. How far the Bessemer operator can go in suppressing the nitrogen content by blowing at lower temperatures will depend upon the skill of alert crews in fast uniform procedure, having available iron of closely controlled analysis and temperature, using well-insulated ladles and all similar aids. This whole situation is subject to further study and development.

PHYSICAL PROPERTIES

The earlier portions of this paper made no effort to describe the general aspects of existing Bessemer plants or operation thereof, the intent being merely to point out wherein modern requirements call for modification of existing facilities and operating methods. Likewise, in referring to physical properties it is considered illogical and impracticable to discuss the general subject in full, but it is desired to point out that the "modernizing" of the physical properties of Bessemer steel resolves itself into the task of understanding and evaluating influences upon those properties, of establishing control of such influences toward improved uniformity with placement of the properties at desired levels. The whole situation further narrows itself largely into considerations bearing upon hardness, embrittlement, and aging. The subject is much too complex for lengthy discussion here, involving the effects of phosphorus, oxygen, nitrogen and probably in more minor ways a host of other chemical and physical factors. It is possible, however, with no great difficulty to gather observations that contribute to knowledge and understanding.

As an interesting example of this statement, there are included here tensile tests of hot-rolled Bessemer steel, in two groups, one group pulled at room temperature and another group at 500°F. to produce a thermally aged condition. The tensile results are plotted against nitrogen contents in Fig. 12. It is to be noted that the normal tensile increases appreciably with increasing nitrogen. Thermal aging raises the ultimate tensile strength and this effect increases sharply with increasing nitrogen. There is good reason to believe that work-hardening, embrittlement by cold-work, time aging, and similar phenomena parallel in relationship to nitrogen content the thermal aging here shown.

SUMMARY

Since the conclusions of this paper have been stated as the presentation of the sub-

ject matter progressed, little remains except to say that for reasons largely economic the Bessemer process of steelmaking developed rapidly in its early history to a figure of large tonnage. It has receded steadily from its peak, owing to reasons both economic and metallurgical. The decline of the Bessemer process probably has gone somewhat further than is justified by present economic considerations, and these considerations will tend to sustain and perhaps even increase Bessemer production in coming years.

The extent to which economic factors may become effective in maintaining or improving the standing of the Bessemer process depends upon the extent to which manager, operator, and metallurgist will exert themselves toward good design, good maintenance, and good control. The future of the Bessemer process can be bright indeed, and whether it is so or otherwise will rest not with the characteristics of the process but with the will and intent of those who operate it.

ACKNOWLEDGMENT

To the many members of the organization with which the author is associated, who have assisted him with willing and enthusiastic effort in study of the Bessemer process and in preparation of the present paper, he hereby offers his sincere acknowledgment.

DISCUSSION

(E. C. Smith presiding)

J. CHIPMAN,* Cambridge, Mass.—Certain features of the relationships governing the nitrogen content of Bessemer steel can be examined in the light of what has been learned regarding the solubility of the gas in molten iron. At atmospheric pressure pure liquid iron will dissolve about 0.040 per cent nitrogen and the saturation value is slightly increased by increasing temperature. The rate of solution in pure iron is relatively slow, and the normal

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amount contained in Bessemer steel is considerably below the saturation limit. The nitrogen content of the product therefore is governed mainly by factors that affect the rate of solution and is only indirectly affected by those that influence the solubility.

It has been observed that the rate of solution is greatly increased by the presence of a small concentration of silicon in the iron. The residual silicon in the metal is in all probability related to the finishing temperature, although published data on this point are lacking. It seems probable, therefore, that the nitrogen-temperature relationship of Fig. 11 can be explained by the effect of the residual silicon upon the rate of solution of the gas.

E. B. STORY,* Pittsburgh, Pa.—Any one concerned with the manufacture of acid Bessemer steel will recognize the significance and value of the various points discussed by Mr. Graham. As he implies, the Bessemer process grew up with not too much technical help. In its growing stages, the open-hearth process also did not receive too much technical assistance. In recent years, however, a great deal of study has been made of the open hearth, especially the equilibrium phase between slag and metal, and it occurs to me that a study along similar lines of the acid Bessemer converter might develop most useful information.

My company is not old in Bessemer operations but we have done considerable investigative work, and our findings rather confirm those of Mr. Graham.

Overblowing and excessively high metal temperatures are undesirable. We have made test heats where the metal was overblown and others where the metal was not overblown but raised to excessive temperatures in the vessel. Critical testing of the material broadly indicates that excessive metal temperature has more effect than overblowing. It should be recognized, however, that the very act of overblowing will, in itself, tend to produce high metal temperatures.

W. S. SCOTT,† Cleveland, Ohio.—We cannot emphasize too much Mr. Graham's ideas that

a close attention to detail and standardization of practice results in an improved grade of Bessemer steel. With metallurgical attention directed toward the Bessemer process the field of application of Bessemer steel will no doubt be extended, as the inherent simplicity of the process lends itself to an exact duplication of quality difficult to attain in open-hearth practice.

P. F. MUMMA,* McKeesport, Pa.—The author is to be complimented on the clear picture he has drawn of the present plight of the Bessemer process, and the thought-provoking manner in which he has pointed out some of the operating variables that might be brought under more precise control in order to help this process regain some measure of its former importance in the steel industry.

To one unfamiliar with the technical advances made by Bessemer operators and metallurgists during the past few years, the paper might give the impression that Bessemer steel today is substantially the same product as that made 20 years ago, and that a complete revamping of the process will be necessary before it can produce steel able to compete successfully with present-day open-hearth products. That this is not so and, indeed, was not the impression intended by the author, would seem evident from a consideration of the current production of such special Bessemer steels as screw stock, wool wire, leaded steel, corrosion-resistant steel, mechanically capped and fully killed Bessemer grades, etc. Undoubtedly, there is still much room for improvement, just as there is in other steel-making processes, but the very fact that a technical paper like the present one could be prepared is gratifying evidence of the amount of serious thought currently being applied to the manufacture of Bessemer steel.

The dependence of the open-hearth method on an adequate scrap supply is well recognized, and even though the percentage of scrap in the charge is now more frequently 35 per cent than the 50 or 60 per cent used a few years ago, the use of blown metal, or "liquid scrap," in the open hearth, is increasing. As an intermediate step, where liquid blown metal cannot conveniently be transported to the open hearth,

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blown-metal ingots or "synthetic scrap" is being made in considerable tonnage for open-hearth use. This growing use of Bessemer converters as scrap producers for the open hearth, while providing a desirable load for existing Bessemer facilities, tends to assist the open hearth to maintain its present dominant position and may seriously delay the more extensive utilization of Bessemer steel.

Instrumental determination of the "end point" of the Bessemer blow, by photoelectric measurements of the luminous energy of the flame, is an interesting development, which leads one to speculate as to the relative effectiveness and simplicity of this scheme and the spectroscopic methods that again are receiving some attention from Bessemer operators. Several statements in the paper indicate the author's belief that blowing temperature is an extremely important factor in determining quality of Bessemer steel; a feeling that is pretty generally accepted by both practical operators and technical investigators. This leads to the thought that since, for the usual analyses of Bessemer steel, the blower has little difficulty in obtaining a fairly narrow range of carbon content by visual inspection of the flame, perhaps an accurate and direct determination of the temperature of the metal in the vessel would be more effective in controlling manganese efficiency, nitrogen content, and the state of oxidation of the finished steel than is the precise determination of the carbon end point. If this should prove true, it would appear logical to strive for a direct measurement of converter-bath temperature rather than a temperature inferred from flame-luminosity energy, which conceivably might not bear a direct relationship to actual bath temperature. In this connection, a distinct improvement in open-hearth bath pyrometry has been achieved during the past two years, and the adaptation of the principles utilized in this procedure to the Bessemer process is now under study.

Measurement of the temperature of the iron immediately before charging into the converter could be accomplished by use of the same equipment, with perhaps some minor changes in operating technique.

In conclusion, we would like to ask the author whether the photoelectric end-point device would be of assistance to the blower in turning down heats of open-hearth blown metal at carbon contents in the range of, say, 0.25 to 1.00 per cent.

H. W. GRAHAM (author's reply).—Dr. Chipman's comments constitute a constructive contribution dealing with a phase of Bessemer-steel metallurgy in which we are admittedly groping in the dark. If the silicon content of the iron is high, a high nitrogen content of the finished steel is to be expected; but the technique of handling scrap or other cooling additions is sufficiently inadequate to make it likely that blows with initially high silicon will proceed with a higher than average temperature, thereby leading one to wonder whether the high temperature is not the major factor in favoring higher nitrogen content.

It is true, however, that high-temperature blows will also have a higher than normal residual silicon, which is in line with Dr. Chipman's suggestion; but, neglecting the small percentage of very badly handled blows, the range of residual silicon to be expected would fall within the limits of 0.01 to 0.04 per cent even with a considerable variation of blowing and finishing temperature. We wonder if a variation of this small order is sufficient to appreciably affect nitrogen absorption.

In answer to the question by Mr. Mumma, it must be stated that the "electric eye" is not a temperature-measuring device in the sense in which one usually thinks of such instruments. It is a fact, however, that the luminous energy of the flame is dependent upon the temperature of the bath in the converter. Since the photoelectric arrangement records the luminous energy, any increase of temperature causes the recording pen to climb to a higher level on the chart. To date it has not been possible to calibrate the height of the curve in terms of temperature, so that it can be accepted only as an indication and not an actual temperature measurement. Nevertheless, in the hands of an alert operating crew, the "electric eye" does offer great assistance in maintaining more uniform temperatures from blow to blow.

Photocell Control for Bessemer Steelmaking

BY H. K. WORK,* MEMBER A.I.M.E.

(New York Meeting, February 1941)

THE Bessemer process is one of the most interesting methods of making steel. At one time it was by far the most important. In recent years, however, it has steadily lost ground to the open-hearth process. The forces working against this method of steel-making are partly economic and partly metallurgical.¹ In this paper, dealing as it does with the control of the process, the metallurgical factors alone will be considered, although it is obvious that economic factors must play a part in determining the ultimate status of the Bessemer process. This discussion has been limited in another respect—it deals primarily with the acid Bessemer process in bottom-blown converters, although much of the information is applicable to basic and side-blown converters.

The fact that open-hearth steel has superseded Bessemer steel to a large extent has tended to create an impression that Bessemer steel is inferior. As a matter of fact, Bessemer steel is actually superior to open-hearth for many applications.² There are, however, definite metallurgical limitations to the use of Bessemer steel, resulting largely from two factors: (1) the physical properties conferred by nitrogen and phosphorus, and (2) the variability from blow to blow. These, of course, are not entirely independent, since some of the variability covered in the second item is undoubtedly due to nitrogen. But the variability is also

caused by other factors. One of these is the relatively small size of the Bessemer heats. Because of this, a given shipment of Bessemer steel is more likely than a shipment of open-hearth steel to contain the product of several heats, each with its own distinctive and slightly different characteristics. Added to this is the fact that the refining of Bessemer steel proceeds so rapidly that the timing of the end point is limited to a matter of seconds, whereas the finishing period in the open hearth extends over a period of one or two hours and the timing of the end point may vary by several minutes without seriously affecting the product. There is no doubt that this has contributed to the variability of Bessemer steel and has led to the use of open-hearth steel in many optional applications.

That Bessemer steel may vary is not necessarily objectionable, and it may even prove an advantage, providing a precise control is available to secure the desired qualities for any specific application. With this in mind, a comprehensive research program was undertaken, one phase of which was directed toward securing more accurate control of the blow. The results have been encouraging, and it is the purpose of this paper to describe a method in which modern scientific instruments, based on photocells, are currently being employed to assist the blower.

THE CONTROL PROBLEM

In this day of scientific control of technical processes, where the operating

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¹ References are at the end of the paper.

man has the active assistance of scientific instruments and technologists, the Bessemer process stands out as an anomaly. Here the control depends on just one man—the blower.³ There are available to him various well-known devices for control, such as steaming, scrapping, side-blowing, or regulating the blast, but for this discussion it is more important to consider how the blower knows when to apply these controls.

In starting this work, a rough survey was made to determine how converters were being controlled. Consultations with Bessemer blowers, metallurgists, and operating people did disappointingly little to clarify the situation. The blowers' ideas as to the proper way to control a blow varied widely from one man to another. Some described in great detail what they saw in the flame in the matter of arrests and color changes and what they meant; much of this information has since been confirmed by photocell methods. Others had little to offer: their basic idea seemed to be that if the preceding blow had a skull the next blow should be hotter. Among the metallurgists, and operators also, differences of opinion existed. Suffice it to say that the impression was formed that Bessemer blowing is not too consistently handled—possibly because there have been so few recent publications on the subject that would tend to standardize opinions and practices.

This scarcity of recent publications does not indicate that the Bessemer process has always been neglected. In the early days of the Bessemer development there was a tremendous amount of activity of both practical and scientific nature designed to improve the control of the Bessemer process. The desirability of such control was recognized almost as soon as the process came into use. Boucher⁴ tells how Kelly in his early attempts to control the converter used to take the spittings from the vessel and hit them on an anvil with a hammer. When the particles became malleable the

blow was complete. However, not all of this early work was so crude in character. The spectroscope was one of the first instruments tried for control purposes. F. Kohn,⁵ in 1868, commented on this as follows:

It seems a strange coincidence that spectral analysis and the Bessemer process should have been brought into practice almost at the same moment. There are scarcely any two discoveries which, at the first thought, appear so strikingly related to each other, and which, from the nature of the principles upon which they are based, should be supposed to afford so great a mutual assistance in the progress and development of both.

Nevertheless, in spite of the obvious advantage of analyzing the flame by means of the spectroscope, this method has not lived up to early expectations. T. M. Drown,⁶ in 1871, pointed out that the spectroscope had not been particularly successful in England; it was noted that in Germany the spectroscope served a useful purpose, and this he associated with the longer duration of the blow. This slowed down the changes at the end of the blow and allowed the use of information obtained by the spectroscope. Between 1894 and 1901, W. N. Hartley⁷⁻¹⁰ discussed in great detail the use of the spectroscope for control of the Bessemer blow for both acid and basic processes. In that time the spectroscope was actually losing ground because its use in Germany had started to decline. Today the spectroscope is seldom used; presumably because the spectroscope merely gives qualitative information when quantitative information is needed.

Other methods of controlling the blow were actively studied. Sampling of the blow was attempted in 1873.¹¹ It was accomplished by inserting an iron rod in the bath, removing and quenching it, and studying beads of iron removed from the slag. This was done in conjunction with spectroscopic tests.

Analyses of the gases issuing from the mouth of the converter were studied at an

early date. A. Tamm¹² did some work along these lines in Sweden in 1879. In 1880, C. F. King¹³ analyzed samples of slag and metal during the course of the blow in a fashion resembling somewhat recent studies of the open-hearth process, but in the Bessemer process these analyses were not sufficiently rapid to be of use for control purposes.

The Pottstown Iron Co.¹⁴ in Pennsylvania in 1891 employed on basic converters a method of control that consisted of regulating the quantity of air blown into the converter by operating the blowing engines a predetermined number of revolutions beyond a point determined by the spectroscope.

Eldred's¹⁵ patents of 1906-1907 show a process in which partly burned gases were introduced in the blast to facilitate control, but little use seems to have been made of this method.

G. K. Burgess,¹⁶ in 1917, concluded that it was impracticable to follow the temperature of the blow by sighting an optical pyrometer on the metal. R. Frerich,¹⁷ in 1928, tried to use an automatically recording radiation pyrometer to follow the blow. He observed wide variations resulting from variations in the iron charge and the blast. More recently Swinden and Cawley¹⁸ tried photoelectric equipment to control the blow, and reported unsatisfactory results.

The Bessemer process may be said to have gone through several stages of development. The first period came shortly after the introduction of the process in the eighteen fifties and consisted of a period of intensive scientific investigation with all of the facilities that were available at that time. Today we must acknowledge our debt to the early investigators who laid the foundation for the present practices, which have produced many millions of tons of steel. The second period was one of industrial expansion under the great steel masters. This period was characterized by the combination of small manufacturing units into large ones; the steelmaking

efforts were directed toward producing more steel at a lower cost. In this period, technical interest, in general, was at a low ebb and what little interest there was centered in the more flexible open-hearth process. The last period can be defined roughly as the last 25 years, when scientific interest has again assumed major proportions in the steel industry. While most of this has been directed toward the open-hearth process and the interest in the Bessemer process has been desultory in character, there are indications that attention to the latter is reviving. This is illustrated by the widespread use of the Bessemer process in Europe, the Aston process, studies of dephosphorization of Bessemer steel, McCaffery's investigations, and many others. So the conviction remains in many minds that the Bessemer process can and should continue to occupy an important position among the steelmaking processes.

The references in the preceding paragraphs are by no means complete, but were selected to give a picture of the situation. Appraisal of the earlier work and consideration of the present status of the process have led to the conclusion that better control methods are essential if the Bessemer process is to be employed to full advantage. Four essentials of an adequate control method are:

1. *Speed.* The rapidity with which the reaction takes place makes speed a prime requisite of methods for controlling the blow.

2. *Quantitative Accuracy.* Because of inability to meet the speed requirements, qualitative methods have been resorted to in the past and undoubtedly this has contributed to the lack of uniformity of Bessemer steel.

3. *Reference Points.* Reference points must be known, if the control is to be successful.

4. *Records.* Records allow scientific comparisons and subsequent improvements.

Consideration of these facts brings out the interesting point that the vigorous agitation and rapid reaction that characterize the Bessemer process and make it so

PHOTOCELL CONTROL

The most successful method for control of Bessemer converters has involved the use

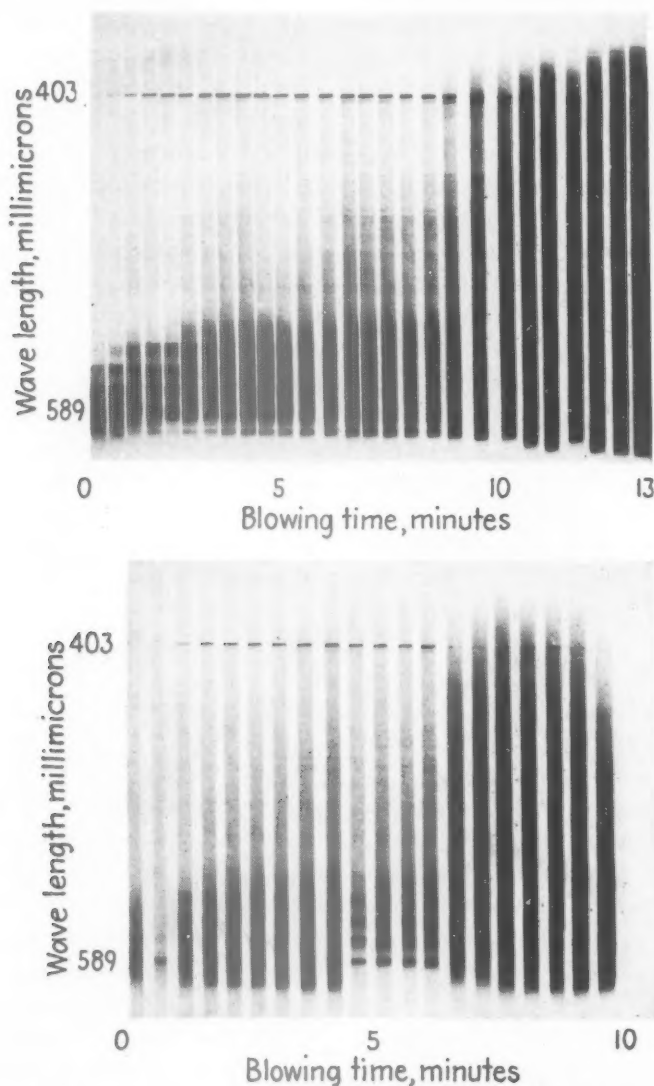


FIG. 1.—SPECTRAL DISTRIBUTION OF VISIBLE ENERGY OF FLAME OF BESSEMER CONVERTER DURING BLOW.

suited for high production are probably its greatest drawbacks from a quality standpoint. Any control, therefore, must, above all else, have speed and accuracy, so that the Bessemer process may compete successfully with the slower but more precise open-hearth process.

of photocells for following the flame. The following pages describe in detail a method¹⁹ now in commercial use.

The selection of photocells to control the blow was predicated on the fact that they were able to give an instantaneous and quantitative record of the flame behavior.

and it was felt that, if suitable reference points could be found upon which to base the control, the method would be far superior to one relying on the human eye. In spite of the speed of reaction of the eye and its ready adaptability to varying conditions, it has one serious fault—it is not quantitatively accurate. This results from certain inherent characteristics of the human eye. It is well recognized in photographic work that accurate estimating of light values is extremely difficult, as is illustrated by the various tables and exposure meters developed for the assistance of the photographer. This is primarily because of the self-adjusting character of the human eye, whereby the pupil automatically adapts itself to light levels over a wide range. In addition the eye varies from person to person, has a limited wave-length coverage, is affected by fatigue and by the physical condition of the individual. Even the most careful selection of blowers for their vision and judgment of small changes—and it is reasonable to suppose that the blowers are probably well above average—leaves much to be desired. Furthermore, the eye produces no permanent record of what has taken place. As a result, it is difficult, if not impossible, to make a scientific study of the flames of a large number of blows to determine the optimum blowing practices. Photocells do not have these objections and they retain many of the desirable features of the human eye.

NATURE OF THE FLAME

In considering the Bessemer flame, it is assumed that its general nature^{2,3} is well known, so an effort will be made to cover merely special characteristics of interest here. This can be done best perhaps by showing a series of spectrograms in Fig. 1 taken at 30-sec. intervals during the course of two different blows. In following these, it should be borne in mind that the equipment employed and the photographic technique affect the results, but for the

purpose of this discussion they are not critical. At the beginning of a blow the spectral energy is rather weak and comprises both lines and bands. As the blow progresses and the carbon begins to burn with a luminous flame the amount of energy increases and a continuous spectrum appears, which almost completely overshadows the line spectra. Toward the end of the blow, the radiant energy decreases rapidly; the rate of drop, however, varies considerably from blow to blow. Over a period of years a tremendous number of spectral lines have been identified in the flame. These have been listed in various publications by Hartley.

Consideration of such spectrograms brings out some important points. One is that the character of the flame and the amount of energy that it emits change during the course of the blow. Furthermore, the series of spectrograms of different blows vary considerably in their general pattern. It is these general variations in the flame that form the basis for photocell control. How this is done will be explained by first describing the equipment and then interpreting the curves that are obtained.

EQUIPMENT

After trying a variety of different photocells and methods for viewing the flame, the arrangement shown in Fig. 2 was tentatively selected for use. The preferred field of the viewing element encloses substantially the whole flame at its maximum size. Naturally, this also includes areas not covered by the flame, but these do not interfere with the flame reading, if suitable precautions are taken in locating the equipment, because of the relatively great intensity of the radiation of the flame. It should be noted perhaps that this arrangement does not restrict the radiating area to a given size, and changes in the flame size affect the readings. Under these conditions it might be thought that the reading would tell little about the temperature of the flame and perhaps even less about the metal

blown in the converter. However, it so happens that when the flame is at its maximum radiating power, the radiation is related to the temperature of the blown

of a suitable range of response, durability, and uniformity, but it is recognized that other cells can be satisfactorily used. The spectral response of this cell is given in

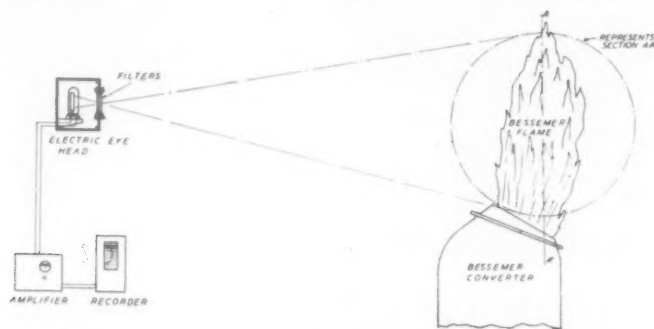


FIG. 2.—POSITION OF PHOTOCELL EQUIPMENT WITH RESPECT TO BESSEMER CONVERTER FLAME.

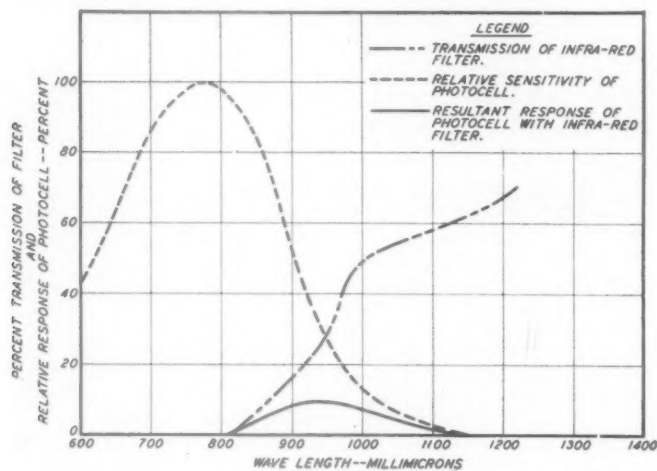


FIG. 3.—RELATIVE RESPONSE OF PHOTOCELL WITH INFRARED FILTER.

metal, so that it is possible to get an approximate indication of temperature from the recorded flame curve. The factors favoring selection of such an arrangement are that: (1) it tends to average out variations in the flame from point to point, (2) the relative size, as well as intensity of the flame, affects the readings, and variations in size are significant, and (3) approximate information on temperature is obtained at the full-flame reading.

The active element for picking up the radiation is a group of three PJ-22 tubes, manufactured by the General Electric Co. This type was selected from the available vacuum tubes and photonic cells because

Fig. 3. Three of these cells are mounted side by side in a housing and set up so the field of view includes the whole flame. Under these conditions, variations in the position of the flame will cause a minimum variation in the reading. The unit is set up about 60 ft. from the converter; the exact location, of course, is controlled by mechanical conditions in the mill, such as: (1) convenience of mounting on parts of building, (2) possible interference by cranes or smoke, (3) exclusion of other Bessemer flames, the sun, and the sky from the field of view, (4) ease of servicing, and (5) a variety of other considerations related to the physical surroundings. It is by observ-

ing these precautions that the effect of the surroundings on the readings is held to a minimum. The response of the cells is amplified and recorded with equipment

evident when an infrared filter is used, but with certain other filters the changes are not nearly as pronounced, and may disappear entirely. Furthermore, the selection

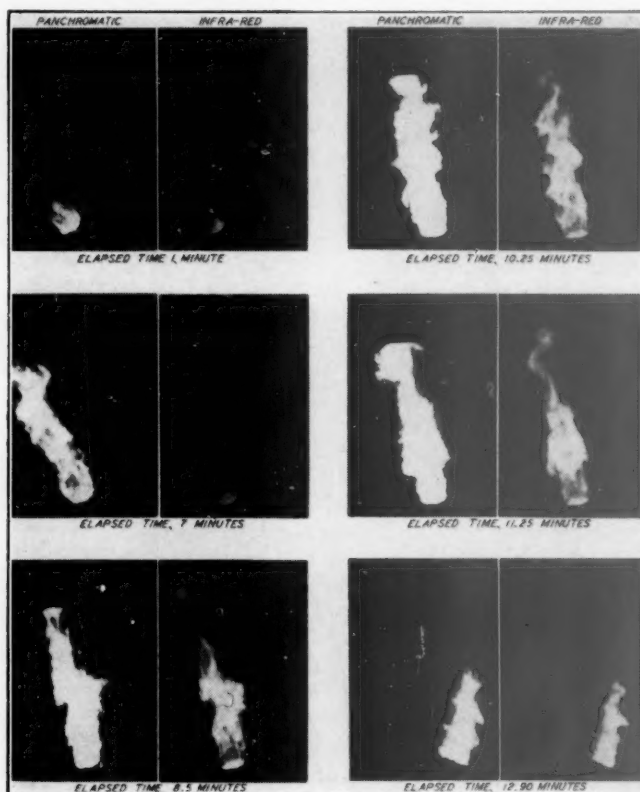


FIG. 4.—COMPARISON OF PANCHROMATIC AND INFRARED PHOTOGRAPHS OF THE BESSEMER FLAME.

shown in Fig. 2, so that there is available, so to speak, an autograph of each blow. The importance of this written record cannot be overemphasized, for it was this that made possible a scientific study to determine the best blowing conditions—a thing that could not be done when the changes in the flame were merely qualitatively recorded in the memory of one man.

In order to use the photocell control most effectively, it is desirable to employ filters on the viewing element. Approximately 80 different individual filters were tried, with many combinations, and it was observed that the filters noticeably altered the trace of the flame curve. For example, the effect of steaming a blow and the flash-up at the beginning and end of the blows are clearly

of the filter has an influence on the clarity with which the end point of the blow is shown. Hence the selection of the filter is very important. To date, two arrangements have been employed most extensively. The first included an infrared filter of which the transmission curve is shown in Fig. 3, together with the response of the photocell and the resultant photocell filter combination. The infrared filter has the advantages that: (1) the reading is less influenced by smoke or steam between the flame and the photocell; (2) the readings are less influenced by daylight; (3) steaming and the end point are clearly shown.

When the infrared filter was first used, the difference in response from other filters was noted. A question was raised as to

whether the infrared radiation of the flame, which was invisible to the blower, followed the same general pattern of the visible flame. To answer this, a series of photo-

by the photoelectric "eye" and the human eye are substantially equivalent.

Despite the advantages of the infrared filter, it showed certain unfavorable fea-

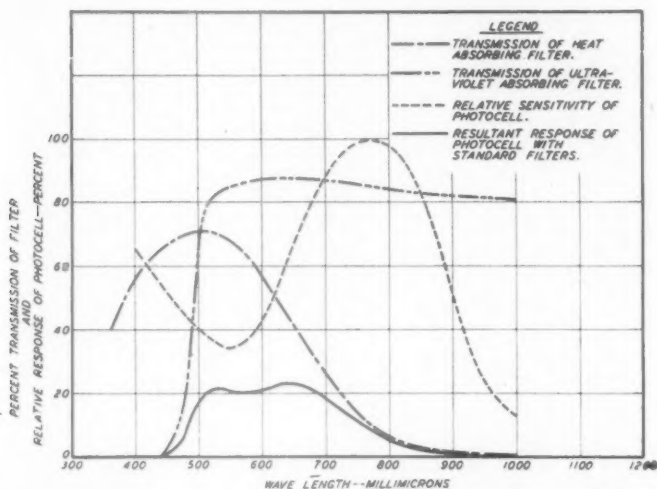


FIG. 5.—RELATIVE RESPONSE OF PHOTOCELL WITH STANDARD FILTERS.

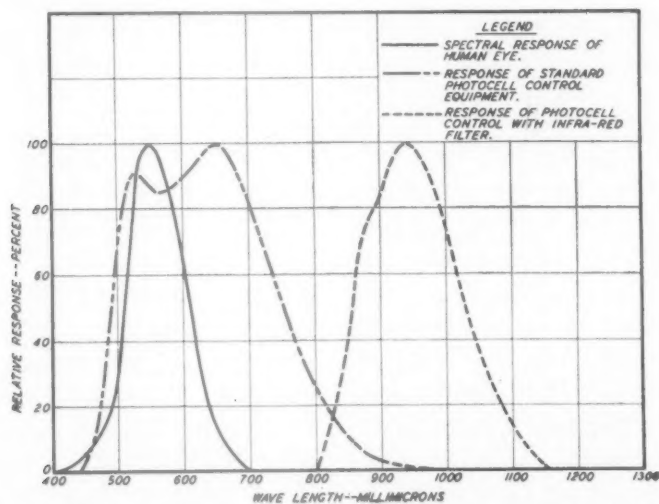


FIG. 6.—SPECTRAL RESPONSE CURVES OF HUMAN EYE AND TWO MODIFICATIONS OF PHOTOCELL CONTROL.

graphs was taken simultaneously in the infrared and visible regions throughout the blow (Fig. 4). Allowing for the recognized limitations in this comparison due to the sensitivity of the plates and paper, and the fact that the relative exposure was not identical, it is apparent that the flames seen

tures when an attempt was made to indicate the end of the blow by an automatic buzzer signal; therefore later it was replaced by a combination of two filters, one of which can best be designated as a heat-absorbing filter and the other as an ultra-violet absorbing filter. This combination is

now used regularly in the mills and will be referred to in this paper as the "standard photocell filter combination." Transmission curves of the filter and the resultant re-

for it is confidently believed that with increasing knowledge of the subject it will be possible to select an even more satisfactory combination.

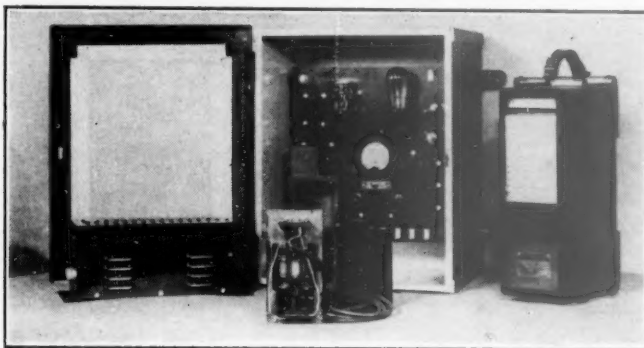


FIG. 7.—BESSEMER CONTROL EQUIPMENT.

Note viewing head with three photocells in foreground; amplifier back of it and recorder to the right.

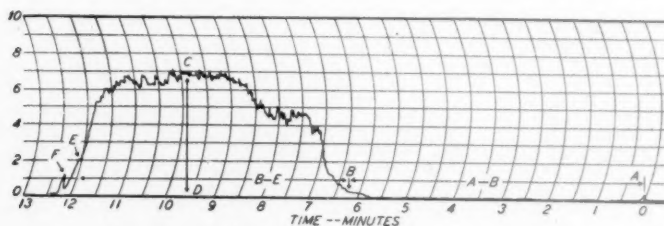


FIG. 8.—SIGNIFICANCE OF THE FLAME CURVE.

A, start.

A-B, silicon blow.

B-E, carbon blow.

C-D, height of curve.

E, end point.

F, flashback.

sponse of the photocell filter combination are shown in Fig. 5. The differences between this arrangement and the one using the infrared filter are that: (1) steaming causes a less pronounced drop in the radiation curve, and (2) the end point falls lower on the curve and varies less in its relative position from blow to blow.

In order to show how the response of these two modifications of the photocell control compare with the human eye, the response curves are compared in Fig. 6. The infrared unit covers a range outside the range of human vision, while the present standard combination extends over the range of human vision and into the infrared.

It probably should be mentioned that, while a workable combination is now available, the study of other filters is continuing,

The basic equipment required for the photocell control unit is illustrated in Fig. 7. The viewing head with the three photocells is shown in the foreground; the amplifier is back of it and the recorder is at the right. These are all well-built pieces of equipment designed for mill service, and they have been giving satisfactory results in the plants for about two years.

THE FLAME CURVE AND ITS INTERPRETATION

To be useful, the equipment for measuring and recording the flame radiation during blowing must give information that can be interpreted and related to certain reference points, thereby showing how to control the blow. To illustrate how this is done, a

typical flame curve made by the equipment described is given in Fig. 8, which will be used to indicate what is now known about its significance and how it is employed.

increase is to be expected, since high silicon contents require a greater amount of oxygen for oxidation and, since there is a relatively constant air flow, it requires a

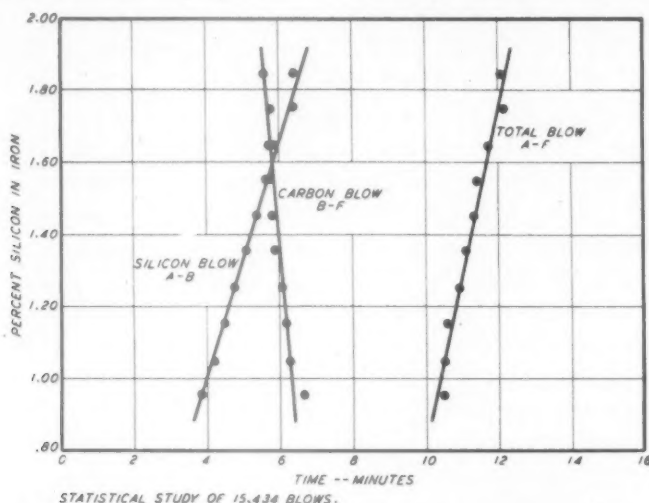


FIG. 9.—EFFECT OF SILICON IN IRON ON BLOWING TIME.

Start of Blow

The point marked *A* is the start of the blow, and because the charts obtained from the recorder read from right to left it is at the extreme right of the figure. Its presence is indicated by a slight rise in the curve, which is caused artificially or by the flame impinging on the wall. For various studies involving blowing time this is an important reference point.

Silicon and Carbon Blow

The period of low flame intensity marked *AB* is generally referred to as the silicon blow because to a large extent the silicon burns out during this period, and *BE* is called the carbon blow for similar reasons. The relationship between the time *AB* and the amount of silicon in the iron is given in Fig. 9, which summarizes a statistical study of about 15,000 blows. It is to be noted that as the amount of silicon increases the time of the silicon blow increases, the carbon blow decreases, but the over-all length of the blow increases. That the time of the silicon blow and the total blow should

longer time to remove the silicon. The explanation for the shortening of the carbon blow *BE*, which accompanies this change, is not so obvious. However, of several possible explanations, perhaps the simplest is most satisfactory. Gas-analysis studies of a preliminary nature of the exhaust gases from the converter seem to indicate that appreciable quantities of carbon monoxide and carbon dioxide are emitted during the silicon blow (Fig. 10). This suggests that the separation between the carbon blow and the silicon blow is not as clear cut as the flame curve might lead one to assume. It also suggests that silicon may repress the luminosity of the flame curve until the silicon is reduced to a fairly low value. Hence with the longer silicon blow more carbon could readily be removed in this period of low flame intensity and the carbon blow shown in the curve would be shorter. Unfortunately, this simple explanation is probably not the whole story because of certain observed temperature effects, which may or may not be related to the silicon content. Nevertheless, this relationship between the flame curve and the silicon of

the iron is being used by the blower to help control the blow.

Height of Curve and Temperature

The maximum height of the curve *CD* furnishes information about the blown metal temperature. A statistical study of over 8000 regular sulphur blows showed a relationship between *CD* and temperature, and indicated that the higher the maximum reading of the flame curve, the higher the blown metal temperature. However, the coefficient of correlation between these results is comparatively low, being 0.17, indicating that height of the curve is not a precise measure of temperature. Part of this may be due to the temperature measurements but it is known that the height of the flame curve is affected by other variables; some of them are well recognized. One is the condition of the nose of the converter. The size of the opening, as determined by deposits formed at the mouth of the vessel, affects the results by its influence on the shape of the flame. As a matter of fact, the readings obtained when the nose is new may vary so much from those obtained from a worn and large one that it may become necessary to change the resistance units in the amplifier to keep the readings at a reasonable point on the chart. The number of tuyeres blanked and the air pressure also have an effect, which probably could better be characterized as the effect of changes in the volume of air going through the converter. These variations are gradual in their effect or where they are not gradual they are known to the blower. This means that in any small series of blows the relation between the height of the curve and the temperature is more consistent than is indicated by the coefficient of correlation. As a consequence the blowers are able to use the height of the curve to guide them in handling the heat. In Fig. 11 are shown three successive blows, which were deliberately blown to give metal of widely varying temperature. The height *CD* was propor-

tional to the temperature of the metal tapped, and this is characteristic of almost any small series of blows. This indication of relative temperature is one of the benefits from the photocell control of Bessemer steelmaking, because of the effect of temperature on the nitrogen content of the steel.

This discussion has dealt with the relation between temperature and the height of flame curve and has merely indicated its relation to nitrogen in the steel. Before discussing the nitrogen problem, it is desirable to consider certain exceptions to these relationships. The first exception can be obtained when the iron temperature and the silicon are both unusually high. Under such conditions the flame curve does not rise to give the typical carbon blow while silicon persists even to the end of the blow. The unusual shape of the curve is related no doubt to an effect of silicon in reducing the luminosity of the flame. It is, of course, obvious that a record of this type is useful because it indicates an unusual condition, which for many applications would be grounds for suspicion that the blow was unsuitable. Another interesting effect is obtained when the blow is steamed—which is sometimes done to cool a hot blow, although whenever possible it is avoided because of a suspected detrimental effect on quality. This is illustrated by curves in Fig. 12. During steaming the flame curve is definitely suppressed, but, as mentioned earlier, the extent of this is dependent on the particular filter used in the photocell unit. The fact that the steaming is now recorded for each blow makes it possible to study the practices of the individual blower and to relate the steaming practice to steel quality. Such studies have been made and it was indicated that steamed blows may be inferior to unsteamed blows. However, that cannot be accepted as proof that steaming is detrimental, since this practice is applied only to blows that are already too hot. Also, a

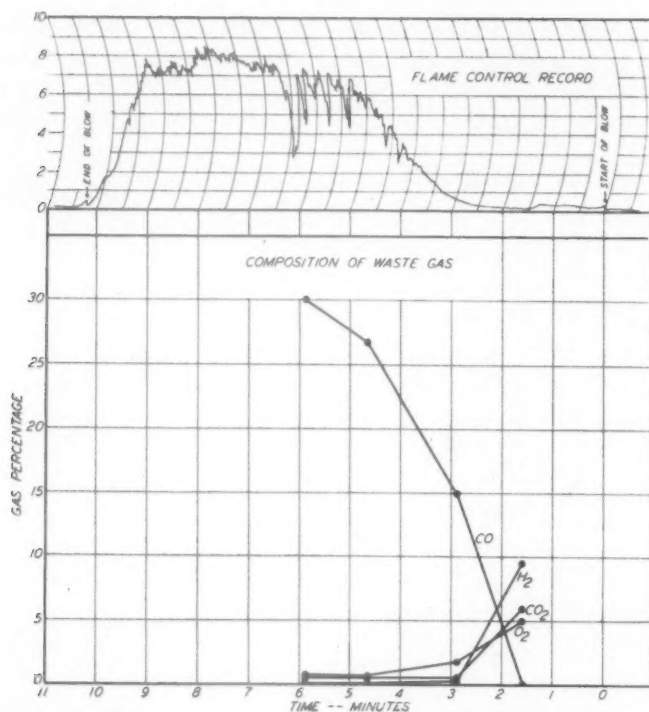


FIG. 10.—PROGRESS OF BESSEMER BLOW INDICATED BY PHOTOCELL CURVE AND ANALYSIS OF EXHAUST GASES.

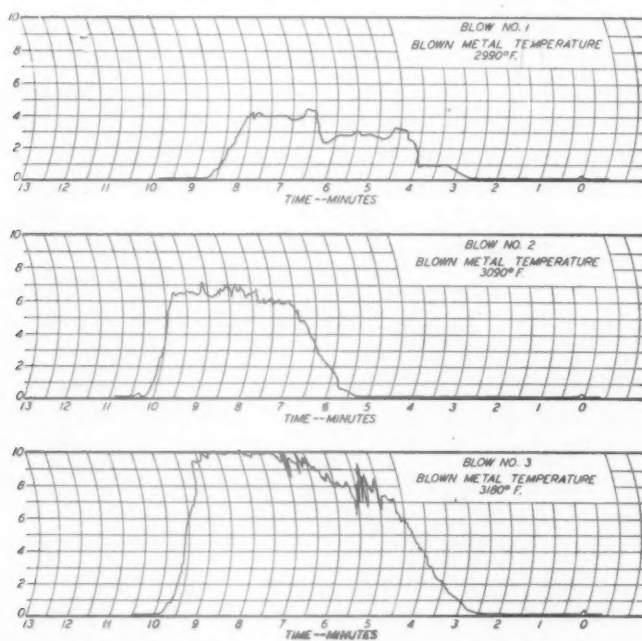


FIG. 11.—RELATION BETWEEN BLOWN-METAL TEMPERATURE AND FLAME-CURVE HEIGHT.

similar relationship has been indicated for the addition of scrap, a practice that by itself would hardly be suspected of a detrimental effect on quality. Hence

of accelerated aging. Graham and Case²⁰ have related the work-brittleness of steel to nitrogen. Damping tests similar to those described by Case²¹ on two steels of similar

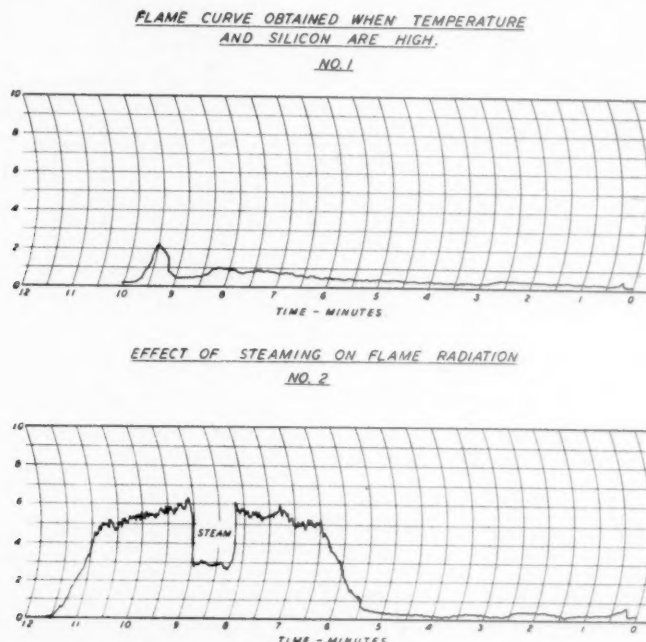


FIG. 12.—EFFECT OF HIGH SILICON, HIGH TEMPERATURE, AND STEAMING ON FLAME CURVES.

this point is going to require additional clarification.

While it is not the purpose of this paper to discuss in any great detail the relationship between the nitrogen content of Bessemer steel and its characteristic properties, the subject is of sufficient interest to justify a brief review. Nitrogen undoubtedly is one of the more important constituents in Bessemer steel, although not much attention has been given to it until recently.^{1,18,20} Nevertheless, it is believed that nitrogen is largely responsible for hardening and embrittlement on cold-working, blue brittleness, low temperature brittleness, and strain-aging—the properties that to a marked degree distinguish Bessemer steel from open-hearth steel. Graham¹ has shown the relationship between nitrogen in Bessemer steel and the difference between high-temperature and low-temperature tensile tests, which may be considered a form

composition, except for nitrogen, have shown different rates of aging. However, despite the many indications pointing in this direction, it is difficult to prove rigidly that the nitrogen alone is responsible for all these phenomena; some investigators believe that the effects ascribed to nitrogen in the foregoing paragraphs are caused by nitrogen in conjunction with other constituents or even entirely by the other constituents alone. The subject is further complicated by the fact that the addition of aluminum, titanium, vanadium, and zirconium causes a tremendous change in the properties mentioned, and it is difficult to separate the effects of these materials on the nitrogen from their effects on oxygen and carbon. The problem is a large and complicated one, but for purposes of this paper the significant fact is that nitrogen is considered to have a most important effect on the properties of the steel.

It has been indicated that the nitrogen content is related to the temperature of the blown metal and it is interesting to speculate as to how the nitrogen is absorbed by

tent of the finished Bessemer steel, for the solubility of nitrogen in the iron even at reasonably high carbon values is considerably higher than that found in the Bessemer

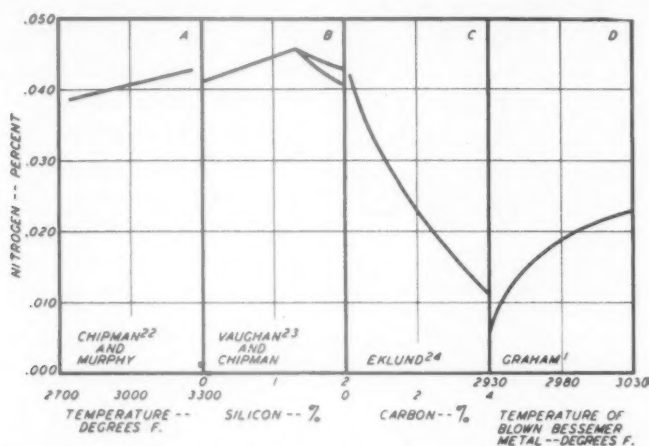


FIG. 13.—SOLUBILITY OF NITROGEN IN STEEL AS AFFECTED BY VARIOUS FACTORS.

the steel. During the course of the blow the nitrogen increases. Nevertheless, the final nitrogen in Bessemer steel is considerably under the saturation value of nitrogen in pure iron at steelmaking temperature, as determined by Chipman and Murphy²² and shown in Fig. 13a. These values are more than twice as high as those shown for Bessemer steel by Graham¹ in Fig. 13d and are not nearly as much affected by temperature. This would indicate either that some material is interfering with the solution of the nitrogen or that equilibrium conditions are not reached. Considering first the possibility that silicon affects the equilibrium condition, Vaughan and Chipman²³ have indicated (Fig. 13b) that silicon has an effect on the equilibrium values but hardly enough to seriously affect the nitrogen content of Bessemer steel. Insofar as carbon is concerned, Eklund²⁴ has found (Fig. 13c) that carbon has a marked effect on the solubility of nitrogen in iron and steel. This no doubt indicates why pig iron has a relatively low nitrogen content regardless of the temperature. However, by itself the carbon content can hardly be said to determine to any great extent the nitrogen con-

steel. It is difficult therefore to escape the conclusion that the equilibrium conditions have not been reached and that factors controlling the rate of reaction are more important than the equilibrium conditions. At the moment it appears that the effect of high temperature is to increase the rate of solution of the nitrogen, although it is apparent that other factors also may play a part in the final results. For example, Vaughan and Chipman²³ have shown that silicon affects the rate of solution of nitrogen in iron but temperature has little effect. To date, however, the effect of silicon on the nitrogen content of Bessemer steel has not been demonstrated satisfactorily. Since the approximate temperature is known, and appears to be related to the nitrogen, regulation of temperature is used as a practical nitrogen control. Another factor, length of the blow, also affects the nitrogen content, and this will be discussed later.

The question of how the nitrogen exists in the steel is of general interest. If the nitrogen merely dissolved, the amount would be determined by the first power of the partial pressure²⁵ and its solubility

would decrease with increase in temperature. Actually it increases with the temperature and is proportional to the square root of the pressure. This indicates that the

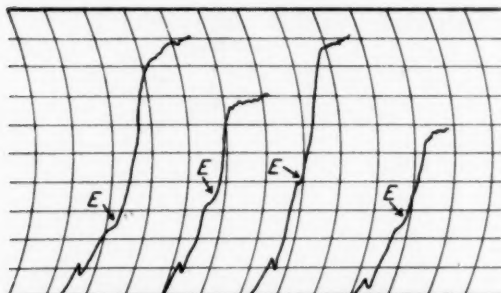


FIG. 14.—TYPICAL END POINTS FROM PHOTO-CELL CURVES.

Note how prominence and position vary from blow to blow.

nitrogen is not present to an appreciable extent as an ideal solution, but is present in a compound involving one atom of nitrogen. It has been suggested that it may be present as Fe_2N , Fe_4N , Fe_6N or Fe_8N , although suggestions have also been made that the nitrogen is in the form of compounds, which include elements such as silicon, or carbon, or combinations thereof, since the behavior with change in temperature is not what would be expected for the simple iron nitride.

This subject of nitrogen has been given a considerable amount of attention here because it is considered one of the important constituents in Bessemer steel. The fact that the photocell control, because of information derived from the height of the flame curve, is helping to regulate the nitrogen is one of the factors in its favor. However, lest there be a misunderstanding, the subject of phosphorus should be mentioned here. Many of the effects attributed to nitrogen in this paper can be caused in part by phosphorus. The practices described here do not control the phosphorus, and other methods of control must be used to deal with that element.

End Point

As the flame falls at the end of the blow in Fig. 8, an arrest *E* occurs. It may vary

considerably in shape and position, depending on the steelmaking practice and the filters used in the flame-control equipment. Some typical examples are given in Fig. 14. One of the factors that affects the position of the end point is the sulphur content of the steel, for high-sulphur blows containing added sulphur show a lower end point than regular sulphur blows. On the other hand, residual sulphur over the range of 0.030 to 0.050 per cent have no appreciable effect on the end point. This influence of sulphur, coupled with thermodynamic studies, has led to the belief that the formation of carbonyl sulphides may possibly be responsible for the arrest in the flame curve.

It has become accepted practice to refer to the beginning of this arrest in the curve as the end point because it has served as a guide to indicate when the blow was ready to turn down. The fact that this arrest occurred regularly at about the same position when blowing conditions were constant made it natural to consider this a natural reference point; in fact, it has assumed a rather mysterious and important significance. By mysterious is meant that its meaning and cause are not clearly understood, but since its use has given good results it is considered important. More recently, when an automatic timer was installed, it was necessary to use a certain fixed flame intensity to start the timer. A definite effort is made to regulate the blowing conditions so that this point shall occur approximately at the regular end point.

Assuming, now, that there has been established a certain fixed point near the end of the blow that indicates a definite point in the progress of the blow, it is necessary to determine specifically when the blow should be turned down for a particular grade of steel. Theoretically, it would seem proper to meter a definite and predetermined amount of air or oxygen through the metal to complete the blow. This has not

proved practical. Variable air leakage in the lines and at the wind box prevents accurate measurement of the air going through the molten metal. Even if this difficulty did not

tory, providing certain corrections are made.

The corrections that are now made in the timing of the afterblow are based on the

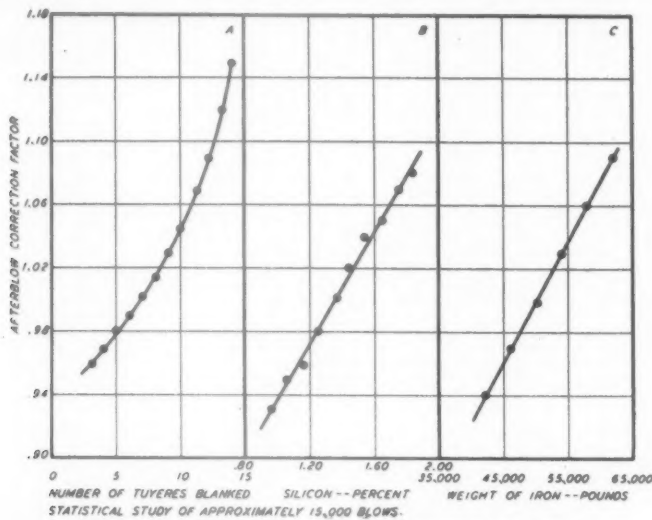


FIG. 15.—AFTERBLOW CORRECTION FACTORS.

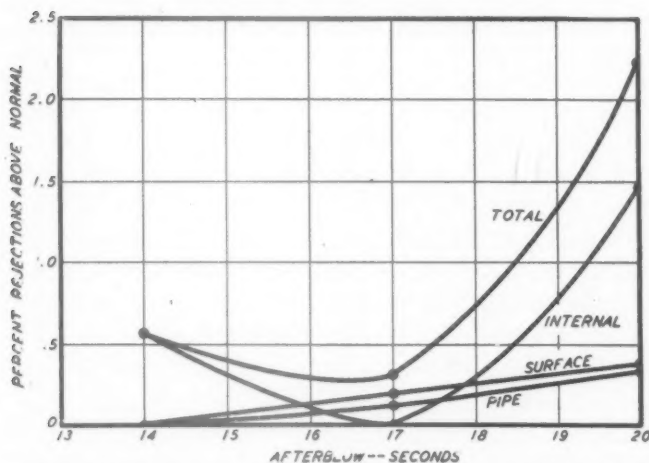


FIG. 16.—REJECTIONS OF BESSEMER STEEL RELATED TO TIME OF AFTERBLOW.

exist there would remain the problem of securing accurate measuring equipment for such large volumes of gas. As a consequence, an approximation was adopted, based on an assumption of a reasonably constant air flow, which is known to be not strictly accurate. This consists of allowing a predetermined number of seconds to indicate when the blow for any particular grade of steel should be turned down. For all practical purposes it has proved satisfac-

number of tuyeres blanked, the silicon in the iron, and the weight of the charge. The number of tuyeres naturally affects the air flow. The effect of silicon is less obvious, but in some way this may be related to the apparent effect of silicon on the flame luminosity. The effect of the size of charge is self-evident; less oxygen is required to blow a small charge than a large one, and this would affect the afterblow proportionally. The magnitude of the corrections now

being used in one plant is shown in Fig. 15, but it is necessary of course to work out these corrections to fit the practice in any particular plant.

of information would eventually tend to standardize these practices.

It is pertinent to consider briefly what the control of the end point signifies metal-

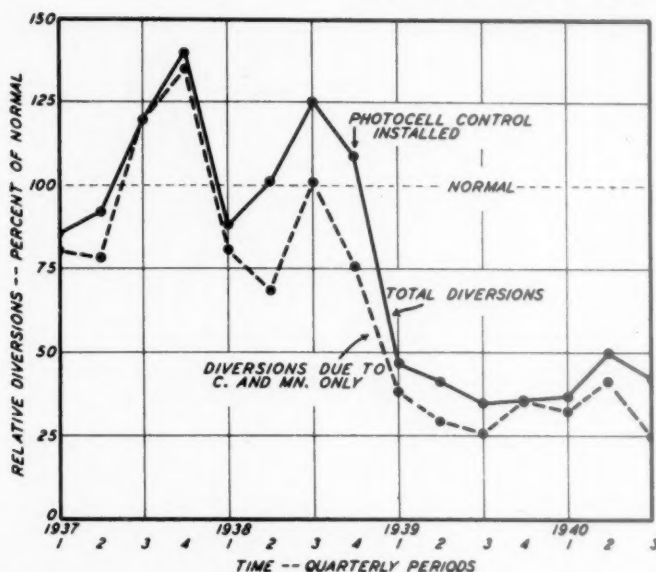


FIG. 17.—EFFECT OF PHOTOCELL CONTROL ON NUMBER OF HEATS DIVERTED.

The number of seconds from the end point until the blow is turned down is called "afterblow," *EF* in Fig. 8. The point *F* is generally referred to as the flashback or end of the blow, and is caused artificially or by the converter flame impinging against the shield on the walls of the building. With certain filter combinations this disappears, but since it is a valuable reference point for checking the afterblow of finished blows a special effort was made to select a filter combination that showed it clearly.

As has been mentioned, each type of steel requires a specific afterblow, which is determined by statistical studies of the variations in yield and quality with the time of afterblow. Typical curves for screw steel, to cite one example, are shown in Fig. 16. These indicate the relation between the length of afterblow and the etch-test rejections, pipe, surface quality, and total rejections. It is obvious that in another plant local conditions might set up requirements for an afterblow of somewhat different duration. Further study and exchange

lurgically. Obviously, it should control the oxidation of the metal. This is further reflected in the carbon and manganese content of the finished steel. Preceding the use of the control, the number of diverted heats ran higher than after the control was installed; heats now are seldom diverted for carbon or manganese, although the sulphur and phosphorus diversions are not affected. This is shown in Fig. 17.

Length of Blow

The various factors that affect the length of blow *AF* have been indirectly indicated in the course of the discussion of the flame curve but will be briefly reviewed here. They are: (1) weight of charge, (2) silicon of charge, and (3) air flow (pressure and tuyeres blanked).

The importance of these factors to the productive capacity is apparent, but there is also an effect of blowing time on the nitrogen content of the steel. This is shown in a statistical study of some 500 blows, illustrated in Fig. 18. There is a definite

relation between blowing time and nitrogen. At first it was suspected that silicon of the iron, which has an effect on the length of blow, might be responsible for

regulating the charge to a greater or less extent—no provisions normally are made to correct the slag during the course of the blow. The slag is treated merely as a collec-

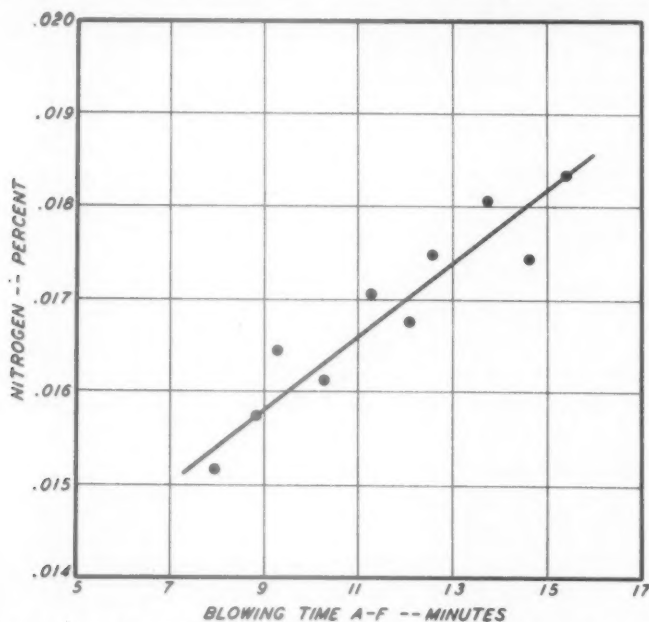


FIG. 18.—RELATION BETWEEN BLOWING TIME AND NITROGEN CONTENT.

this, but studies showed no such relationship. It was concluded therefore that the other factors affecting blowing time must be responsible. That variations in time should affect the nitrogen content is to be expected. As indicated previously, the absorption of nitrogen has in all probability not reached equilibrium and anything giving the reaction more time would cause it to approach equilibrium more closely, thereby resulting in higher nitrogen values.

SLAG

No discussion of a steelmaking process would be complete without some comment on slag conditions. The various relationships between C, Mn, Si, and O₂ in the metal and the slag have been reported by Schenck²⁵ and although more recently determined constants require some revision of his data the latter illustrate the reactions that are taking place. In the Bessemer process the slag control consists merely in

tion of waste products, but its presence must be taken into account, for example, in deoxidation, dephosphorization and duplexing, where the slag, if not removed, will take part in the reactions with a detrimental effect on efficiency.

SUMMARY

A method of controlling the Bessemer steelmaking process by means of photocells is described. This practice gives a rapid and quantitative indication of changes in the flame, which are recorded graphically for each blow. The interpretation of these curves is discussed and procedures for applying the control practices are shown.

ACKNOWLEDGMENT

The author is very much indebted to his associates in the laboratory who took part in this work. In addition, he would like to acknowledge his debt to Mr. H. W.

Graham, whose faith in the Bessemer process made this work possible; to Mr. D. R. Loughrey, whose help and encouragement in the early studies had much to do with its success; and to Mr. J. H. Flaherty and his associates, who contributed much when the work was in its development stages.

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A Study of Modern Bessemer Steels

By E. E. MCGINLEY* AND L. T. WOODWORTH,* MEMBER A.I.M.E.

(New York Meeting, February 1941)

DURING the past several years has occurred what, in the light of future events, may aptly be called the rebirth of the acid Bessemer process. The increased attention given to the technical and metallurgical details involved in the production of Bessemer steels has been exceedingly fruitful, and indicates the value of further research and plant development.

In times like these, when the steelmaking capacity of the country is operating at a maximum rate to supply materials for the national defense program, it behooves the Bessemer operator not only to strive to increase production but also to maintain a high standard of quality. The opportunity is ripe, it seems, to recapture fields of application once considered the birthright of Bessemer steels, but supplanted in recent years by open-hearth grades.

This involves cooperation all along the line, from the blast-furnace operator to the metallurgical contact man and salesman. The metallurgist's part in this program involves the study of the many steelmaking variables and the measures necessary to ensure constancy in the finished product. It is equally important that the knowledge gained be disseminated widely to ensure the wise application of Bessemer steels in new fields.

The merits of Bessemer steels for certain work are well understood. The combined properties of good weldability, machinability and stiffness are unique and fully

explain the strong entrenchment of Bessemer steels in certain fields; e.g., skelp for small butt-weld conduit, screw steels machined in automatics, and certain tin-plate applications.

It is the purpose of this paper to review briefly the physical properties of Bessemer steels as contrasted with those of open-hearth steels, to discuss control measures now employed in the making of Bessemer steel, and to consider the advantages derived from the use of these control measures.

PHYSICAL PROPERTIES OF BESSEMER VS. OPEN-HEARTH STEELS

A number of Bessemer blows and open-hearth heats were tested for tensile strength, ductility and impact strength. The steels selected were confined to sections from $\frac{3}{4}$ to $1\frac{1}{4}$ -in. diameter, inclusive, and the carbon content covered was sufficient to yield parallel ranges in ultimate strength for the comparison. Other factors, such as the extent of deoxidation of the steel and variations in chemistry, were kept as comparable as possible.

Machined test pieces of 0.505-in. diameter with an 8-in. gauge length were pulled. The data obtained are shown in Fig. 1, ultimate strength being plotted against carbon content. This graph shows that for equivalent carbon content Bessemer steel has on the average 15,000 lb. per sq. in. greater tensile strength and, conversely, for the same tensile strength Bessemer steel requires on the average 0.14 per cent less carbon. The average phosphorus content for the Bessemer steel was 0.090 per cent,

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while for open-hearth steel it was 0.013 per cent. It would seem that the higher strength is attributable to the higher phosphorus and nitrogen content, although it was not a

impact strength of Bessemer steel is poor in comparison with that of open-hearth steel, but Fig. 4 shows that the two types of steel are fairly comparable in this respect for any

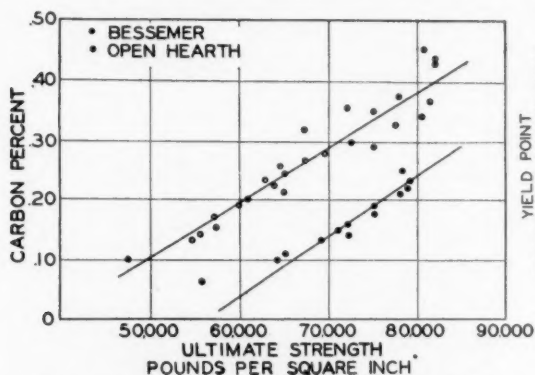


FIG. 1.—COMPARISON OF ULTIMATE STRENGTHS OF BESSEMER AND OPEN-HEARTH STEELS OF SIMILAR CARBON CONTENTS.

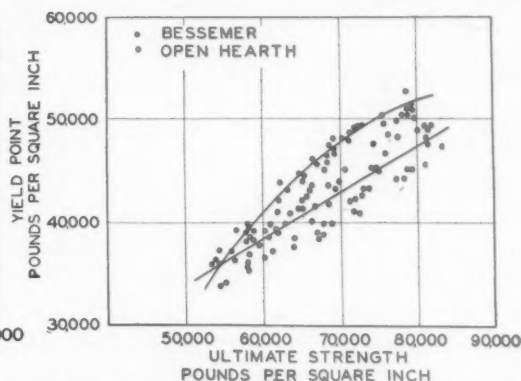


FIG. 2.—COMPARISON OF RATIO OF YIELD POINT TO ULTIMATE STRENGTH FOR BESSEMER AND OPEN-HEARTH STEELS.

part of the present investigation to prove this inference. These tests were made on bars in the as-rolled condition, but a similar set on normalized material gave virtually the same results.

Fig. 2 shows that the ratio of yield point to ultimate strength is considerably higher for Bessemer steel, a valuable characteristic

given ultimate strength; even though the Bessemer steel tends to have a coarser structural grain size because of the deoxidation practice used and conditions in the finishing mill obtained purposely to develop certain other desirable properties. It is known that an increase in grain size adversely affects impact strength.

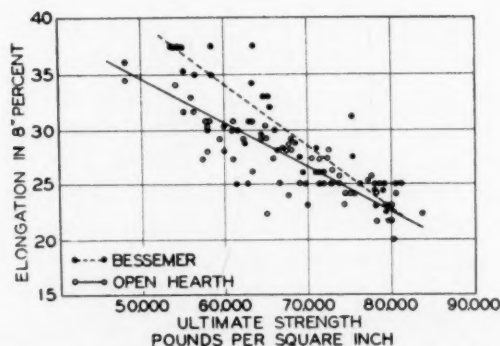


FIG. 3.—COMPARISON OF ELONGATION OF BESSEMER AND OPEN-HEARTH STEELS FOR EQUIVALENT ULTIMATE STRENGTHS.

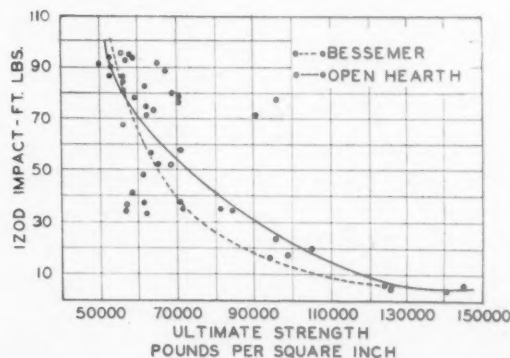


FIG. 4.—COMPARISON OF IMPACT STRENGTHS OF BESSEMER AND OPEN-HEARTH STEELS FOR EQUIVALENT ULTIMATE STRENGTHS.

that probably has not been fully appreciated in the past.

The elongation in 8 in., particularly in the lower range of ultimate strength, is higher in Bessemer steels, as shown in Fig. 3.

It has been generally believed that the

Therefore, it cannot be said that the hot-rolled physical properties of Bessemer steels suffer in comparison with those of open-hearth steels; indeed, some superiority is shown, which should be particularly valuable in certain grades, such as structural steels.

TEMPERATURE CONTROL

The most important features of any steelmaking process are the control of temperature and degree of oxidation. Uni-

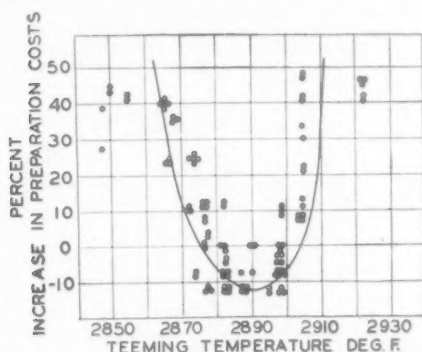


FIG. 5.—EFFECT OF TEEMING TEMPERATURE ON PREPARATION COSTS OF SEMIFINISHED CAPPED BESSEMER STEEL.

form quality goes hand in hand with the uniformity of these factors. This is well recognized by the Bessemer operator and metallurgist, and great advancement in this direction has been made in recent years.

Either extreme of temperature is to be avoided. Low temperatures result in skulls, difficult pouring, and scabby, dirty ingots. A Bessemer plant relies on methodical operation to attain maximum production together with uniformly high quality, and low temperatures with the resulting difficulties upset the smooth operation of the plant.

On the other hand, extremely high temperatures are also detrimental, both to steel quality and economical operation. In the making of rimmed or capped steel, extremely hot heats are to be avoided because of the bad effect on the surface of the semifinished product. A hot heat will have a delayed rimming action, and the lenticular blowholes, particularly in the lower portion of the ingot, will extend almost to the surface. In the subsequent heating and rolling operations these will be exposed and appear as flaws and seams on the semifinished product. In the semikilled grades of steel, hot heats are difficult to deoxidize properly. Mill yields will be erratic and the

surface of the semifinished product will be inferior.

Hot heats are objectionable from a production standpoint also. Delays in

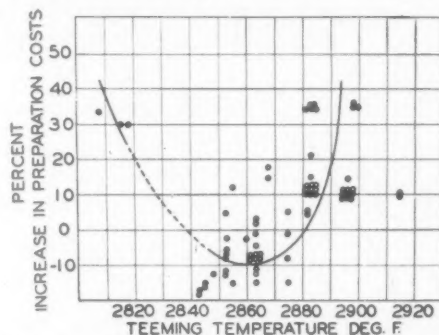


FIG. 6.—EFFECT OF TEEMING TEMPERATURE ON PREPARATION COSTS OF SEMIFINISHED RIMMED BESSEMER STEEL.

stripping caused by sticker ingots, encountered most frequently on hot heats, interfere with the normal flow of steel from the pouring platform to the soaking pits.

The effect on vessel and ladle refractories of extremely high metal temperatures is also well understood. The erosive forces involved, together with the thin watery slags that often accompany hot heats, result in decreased ladle life and an increased number of stopper changes.

A study of the effect of teeming temperature on the preparation costs of the semifinished product for capped steel reveals that under our conditions the optimum teeming range is 2875° to 2900°F., and for rimmed steel, 2845° to 2875°F. Figs. 5 and 6 show this relationship. The zero line on these two diagrams represents the normal cost for preparing the semifinished product for these grades of steel. Any variation from this cost is represented as a percentage deviation. Points lying below the zero line are indicative of "good" blows; that is, blows requiring little preparation to remove surface defects prior to further conversion. Blows with more numerous surface defects, reflected in increased preparation costs, are represented by points lying at various distances above the zero line.

The rapid increase in preparation costs when the teeming temperature deviates from the optimum ranges stated above is clearly shown in these two diagrams. Con-

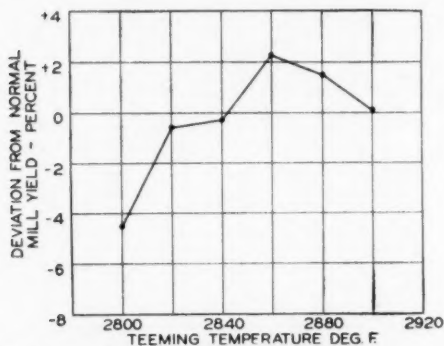


FIG. 7.—EFFECT OF TEEMING TEMPERATURE ON BLOOMING-MILL YIELDS OF BESSEMER SCREW STEEL.

sidering the actual expenditure of money and the loss of time involved in conditioning the semifinished product, the importance of close temperature control, because of its direct bearing on surface quality, cannot be overstressed.

Extensive studies on screw steel have also indicated the existence of an optimum teeming range; namely, 2860° to 2890° F. The influence of teeming temperature on surface quality was found to be the same for this grade of steel as for capped and rimmed steels. In addition, however, the teeming temperature of screw steel exerts a marked influence on the internal soundness of the ingots and the tendency toward piping as reflected in decreasing blooming-mill yields. Most of these steels are made semikilled because maximum machinability can be obtained with steels made by this practice. This necessitates the addition of a deoxidizer to the steel in the molds. The effectiveness of this deoxidizer is directly dependent on the teeming temperature, and the amount necessary will vary for different conditions. Large fluctuations in teeming temperature make it extremely difficult to gauge the proper amount of deoxidizer needed. If a standard amount is added and the steel pours on the low side of the temperature range, the efficiency of the

deoxidizer will be increased so that the resulting ingot may be badly piped and require excessive crop at the bloom shears. Likewise, if the temperature is too high, the

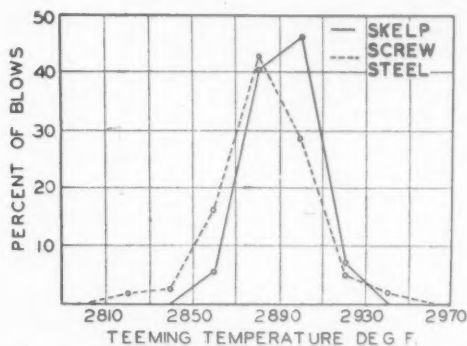


FIG. 8.—DISTRIBUTION OF TEEMING TEMPERATURES FOR BESSEMER CAPPED SKELP AND SCREW STEEL.

efficiency of the deoxidizer is reduced sufficiently to result in an ingot with a spongy top. The effect of teeming temperature on blooming-mill yield is shown in Fig. 7. Each point represents the average yield of a number of blows for a given temperature.

To obtain consistently good yields the teeming temperature must be confined within the range indicated above.

Close cooperation between the metallurgical observer and the blower, has, on the average, caused a great number of the blows to fall within the optimum pouring-temperature range (Fig. 8). These simple frequency curves show the distribution of teeming temperatures for several hundred blows of capped skelp and a similar number of screw blows, selected at random over a period of several months. The temperatures were obtained with the aid of a disappearing-filament optical pyrometer sighted on the stream of a molten steel during the teeming of the ingots. Approximately 87 per cent of the capped skelp blows fell within the temperature range 2870° to 2910° F., while 7.5 per cent were higher and 5.5 per cent fell below this pouring range.

For screw steel the distribution is slightly wider, with 87 per cent of the blows falling within the range 2850° to 2900° F., while

7.5 per cent are higher and 5.5 per cent lower than this range.

Every effort is made to confine the teeming temperatures within the recommended ranges, and, by constantly checking the temperatures from heat to heat, the blower is informed of any variation in temperature, so that, when necessary, corrective measures can be applied on succeeding blows. The blower has at hand several methods for controlling temperature. Variations in the chemical analysis (particularly silicon) and physical heat of the iron must be compensated for if uniform temperatures are to be obtained. The addition of a regulated amount of scrap to the metal bath in the early part of the blow is the best corrective measure for temperature control. During the course of the blow other measures can be taken—the introduction of steam into the blast main as a coolant or the tipping of the vessel for side blowing to increase the temperature. Either of these two methods is to be avoided, since they introduce several additional variables.

OXIDATION CONTROL OF BESSEMER STEEL

The physical chemical reactions between oxygen and the various metalloids when brought into contact at high temperatures are excellently exhibited in the Bessemer process. The oxygen in the air entering through the tuyeres oxidizes the iron to FeO , which in turn oxidizes the silicon, manganese and carbon present in the pig iron, in the order mentioned. While all three reactions are proceeding simultaneously, the speed of reaction for the removal of each element is greatly different. As a result, the silicon and manganese are almost all eliminated before the oxidation of carbon really assumes any magnitude. The excessive oxidation of the iron of the bath is in a sense protected by the presence of the metalloids, carbon, manganese and silicon. As the elimination of these metalloids proceeds, the iron oxide content increases slowly until the end point of the blow is

reached. By this time the silicon has been eliminated and the carbon and manganese have dropped so low that further elimination proceeds less rapidly. As a result, the

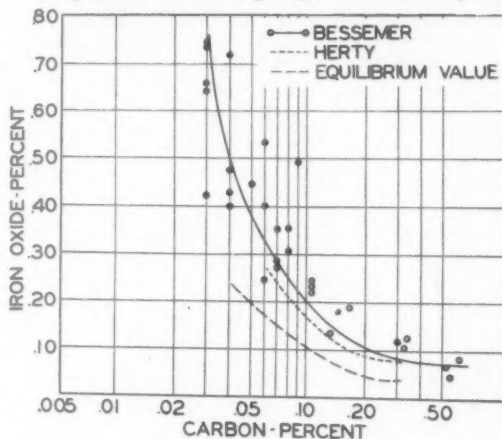


FIG. 9.—RELATIONSHIP BETWEEN CARBON AND IRON OXIDE CONTENT OF BESSEMER BLOWN METAL.

oxide content of the bath begins to increase rapidly and may double in a period of 10 or 15 sec. This rapid increase in oxide content at the end point shows the importance of close control during this period of the heat.

The relationship between carbon and iron oxide in the metal before the addition of any deoxidizer is illustrated in Fig. 9. The data are plotted on semilogarithmic graph paper, a type of plot that has an advantage over a rectilinear graph, in that the lower carbon range is considerably amplified while the higher range is compressed. As we are particularly interested in the low-carbon range, because all Bessemer steels are blown down low in carbon, this type of graph serves our purpose well. This graph, the culmination of preliminary work of this nature, illustrates the rapid increase in oxygen at the end of the blow when the rate of carbon elimination is decreasing. Included also in this chart is a similar curve determined by C. H. Herty, Jr.¹ for basic open-hearth steels, together with the calculated curve for conditions of equilibrium. The rough parallelism of the three curves is interesting, and, as would be

¹ C. H. Herty, Jr., C. F. Christopher, H. Freeman and J. F. Anderson: Control of Iron Oxide in the Basic Open Hearth Process. *Cooperative Bulletin* No. 68.

expected, the displacement, from the calculated equilibrium values, of the Bessemer steel is slightly larger than that of the basic open-hearth steel.

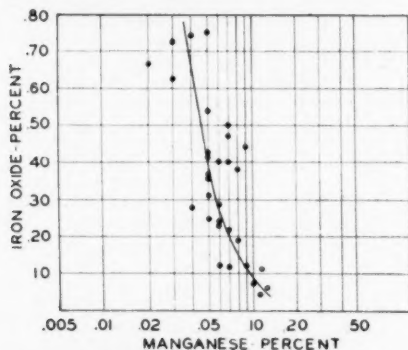


FIG. 10.—RELATIONSHIP BETWEEN RESIDUAL MANGANESE AND IRON OXIDE CONTENT OF BESSEMER BLOWN METAL.

Fig. 10 shows a similar diagram for elimination of manganese from the blown metal.

TABLE 1.—Average Results on Ladle Tests

	Skelp	Screw (S.A.E. X-1112)
Number of heats.....	79	112
Iron oxide, average, per cent..	0.320	0.186
Nitrogen, average, per cent....	0.0096	0.0104

A study of a number of heats of skelp and screw steel (S.A.E. X-1112) has revealed several interesting points. It is the practice at the Youngstown plant to blow screw steel "young" and skelp steel "full." For the uninitiated, these terms mean (1) turning down of the vessel shortly after the end point, and (2) carrying the blow further along. In Table 1 are given the average results obtained on ladle tests analyzing for iron oxide and nitrogen. The tests were taken from the stream pouring from ladle to mold.

The large difference between the percentage of iron oxide in skelp and in screw steel is interesting. While this difference is influenced to a certain degree by the higher manganese specification for screw steel (usually 0.60 to 0.90 Mn as compared with

0.35 to 0.50 Mn for skelp), the biggest factor contributing to the difference is the blowing time after the end point. Iron oxide samples taken before and after the man-

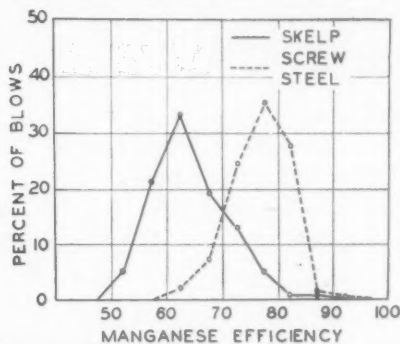


FIG. 11.—MANGANESE EFFICIENCY DISTRIBUTION FOR BESSEMER CAPPED SKELP AND SCREW STEEL.

ganese addition, for both skelp and screw steel, showed that the iron oxide content of the molten steel was reduced approximately 50 per cent by the manganese addition.

This difference in the degree of oxidation of the bath is reflected in the manganese efficiency of the two types of steel. Referring to the simple frequency curves in Fig. 11, it is obvious that the smaller degree of oxidation of the bath in the screw steel results in an appreciable increase in manganese efficiency, and also in a more consistent manganese yield. It can be shown from these curves that for skelp 87 per cent of the blows studied fell within the range of 55 to 75 per cent manganese efficiency, while for screw steel 88 per cent of the blows fell within the range of 70 to 85 per cent manganese efficiency.

NITROGEN IN BESSEMER STEEL

The amount of nitrogen in Bessemer steels and the factors controlling it are being studied. It has generally been thought that the factors governing the amount of nitrogen pickup in blowing are: (1) the length of (a) total blowing time and (b) time interval from end point to turn down; (2) temperature of the blow; (3) carbon content of the bath.

Some experimental work has been done regarding the relation between blowing time and nitrogen content at the Youngstown plant, but so far the results have been

two grades of steel; $\frac{1}{4}$ the number of blows were S.A.E. 1112, the remainder were S.A.E. X-1112. There seems to be a tendency for the lower-sulphur steels to have a

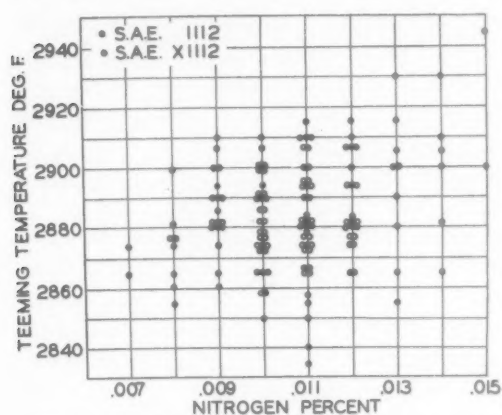


FIG. 12.—VARIATION IN NITROGEN CONTENT OF BESSEMER SCREW STEEL FOR DIFFERENT TEEMING TEMPERATURES.

negative. A sample of this work is given in Table 2.

TABLE 2.—Relation between Blowing Time and Nitrogen Content
CAPPED SKELP, 0.08 PER CENT CARBON, 0.35 TO 0.50 MANGANESE

Blow No.	Roll Scale, Lb.	Over-all Blowing Time, Min.	N ₂ , Per Cent
5833	0	11	0.010
5834	0	15	0.009
5835	1,000	9	0.011
5836	1,000	9	0.010

Assuming that teeming temperature can be directly correlated with the temperature of the steel in the vessel at the turndown of the heat, for a constant ladle addition of ferromanganese, an attempt was made to determine the effect of temperature on nitrogen content. Fig. 12 indicates a slight upward trend in nitrogen content as the teeming temperature increases, but the variation for any given pouring temperature is so large that if the extremes were ignored it would be difficult to discover any trend.

The data presented in Fig. 12 represent

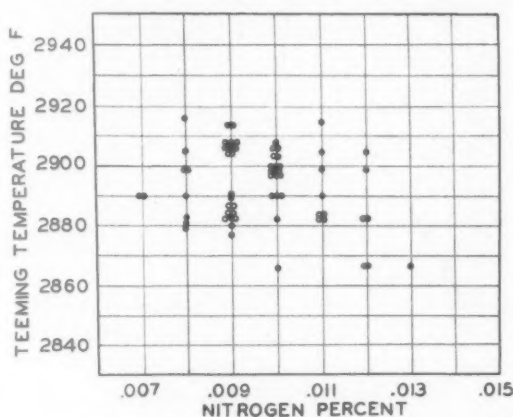


FIG. 13.—VARIATION IN NITROGEN CONTENT OF BESSEMER SKELP FOR DIFFERENT TEEMING TEMPERATURES.

higher nitrogen content, but these blows represent teeming temperatures above the normal. The amount of sulphur present cannot have a marked effect on the ability of the steel to dissolve nitrogen, however, because the nitrogen pickup on skelp, which on the average contained 0.030 to 0.040 per cent sulphur, was of the same magnitude as the nitrogen pickup on screw steel.

Fig. 13 shows the distribution of nitrogen in skelp for the various pouring temperatures. Here again, for the limited number of heats involved, no definite trend could be established.

Frequency curves for the screw and skelp blows involved in this study showing the distribution of nitrogen content are presented in Fig. 14.

Data have been examined on the increase of nitrogen in the bath during the blowing period of publications by Swinden and Cawley,² as well as some reports of subsidiary plants of the United States Steel Corporation, which indicate that nitrogen

² T. Swinden and F. B. Cawley: The Acid Bessemer Process of Steel-Making. *Iron and Steel* (1939) **12**, 387-91, 431-34, 593-99. Also published in *Trans. Marine Engrs.* (1939) **51**, 99-134 and extracts in *Iron and Coal Trades Rev.* (1939) **138**, 502-3, 547-48.

is built up at an accelerated rate during the blow. However, we have been unable to show any marked difference in nitrogen content between "young" and "full" blown steel.

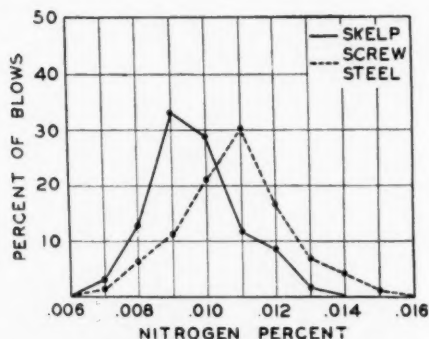


FIG. 14.—DISTRIBUTION OF NITROGEN CONTENT OF BESSEMER CAPPED SKELP AND SCREW STEEL.

The data that have been published and the experiences of different Bessemer plants of the Carnegie Illinois Steel Corporation indicate that different plants produce a slightly different nitrogen range. Thus, one plant may average 0.011 per cent nitrogen and another may average 0.015 per cent. The reasons for this probably are tied up with the individual plant's equipment, raw materials used, and practices.

SUMMARY

The control of temperature, degree of oxidation, and a better understanding of the fundamentals affecting nitrogen content are basic problems, and the purpose of this paper is to attempt to contribute to the general store of knowledge, with the full realization that there is still much to be learned. We know that the technical attention given to the Bessemer process in the recent past at the Youngstown plant has been repaid surprisingly in better quality, increased manganese yield, and greater customer satisfaction.

It is evident that any measures taken to ensure closer control over steelmaking variables will materially aid in the revitalization of the Bessemer process.

ACKNOWLEDGMENT

The authors wish to thank Mr. E. T. Barron, Manager Metallurgical Division, Pittsburgh District, Carnegie-Illinois Steel Corporation, for the data he contributed, and to express their appreciation of the cooperation and assistance given by the members of the operating, chemical and metallurgical staffs at the Youngstown works in the preparation of this paper.

DISCUSSION

(H. W. Graham presiding)

S. L. HOYT,* Columbus, Ohio.—The present paper arouses interest in the factors that control or affect steel quality and the authors are to be commended for an able presentation of their case for Bessemer steels. I believe consumers, by and large, will be willing to stand on the facts, though doubtless they will insist that their own requirements be taken into account. The authors have contributed to this end, but I am convinced consumers will insist on going beyond the present scope of this paper.

Casualty, the Izod values of Fig. 4 appear to indicate good notch toughness—or "impact strength"—and the authors imply that Bessemer steel is comparable to open-hearth steel, even in spite of a less favorable deoxidation practice. In view of present knowledge of notch behavior, it is certain that a more searching study of the Bessemer grades is called for than that reported. To carry this study to a reasonable conclusion, I would suggest determining the effects of zero and subzero temperatures to bring out the temperatures for Bessemer and open-hearth steels, respectively, at which the low level values are encountered. Incidentally, the straight Charpy test is better adapted to such work, though generally it gives lower impact values. It is very likely that the high values of the Izod test are vitiated by an ineffective notch, so that the behavior in pure bending is reflected. Other things being equal, the phosphorus content of 0.09 per cent would be expected to show a difference in the temperature sensitivity, and this point is missed by the authors. It is true that an even greater amount of phosphorus can be used without sacrificing

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notch toughness but the measures taken to ensure this are not mentioned by the authors.

The authors' comments on nitrogen are of interest, though hardly adequate for an appraisal of steel quality. When nitrogen can occur in different forms in steel with different effects on the behavior, reporting merely the total amount misses the important point of how much active nitrogen is controlling the properties. The actual amounts reported are high enough to excite misgivings and it should be profitable, in work on Bessemer steel, to explore the nitrogen problem thoroughly enough to bring this element under adequate control.

The same is true in principle for oxygen, which is reported only as iron oxide though sufficient in quantity to have a metallurgical effect. Both of these elements can be determined fractionally to show how they are associated, and presumably their activity, and hence the method of the fractional vacuum fusion (or comparable procedure), should be a very potent tool for studies of Bessemer steel.

The behavior of steels in strain-aging is a rather critical criterion of the kind of steel under investigation. I have found this method of great value in selecting steels for use and in studying quality of weld metal. It seems certain that many potential users of Bessemer steel would want to be posted on the response to strain-aging, particularly if new applications were involved which at present are using the open-hearth grades.

I should like to refer briefly to Fig. 1, which gives the relation between carbon and ultimate strength for Bessemer and open-hearth steels. The two curves reflect the facts, but it would be far more enlightening if other factors, such as the amounts of phosphorus, nitrogen, manganese, etc., were also taken into account to produce one single relationship. The present method of plotting, while satisfactory for the simple relationship between carbon and strength, still leaves unanswered the question as to why such a difference exists between the two steels.

The authors obviously are well aware of the requirements of their problem to "recapture" fields that have been lost in the recent past. By eliminating doubts, or prejudices, and by developing knowledge of the individual characteristics and properties, and by learning how to

control them, a sound basis would be established to attain the authors' avowed purpose.

E. E. MCGINLEY AND L. D. WOODWORTH (authors' reply).—Many of the points brought up by Dr. Hoyt would certainly serve as a basis for further research work in the field of Bessemer steels.

The physical testing data presented in the paper, comparing open-hearth with Bessemer steel, were offered with the thought in mind of indicating the possibilities of Bessemer steel substitutions for many of the commonplace applications, which often are unnecessarily specified as open hearth. We realize, however, that, because of the many steelmaking and finishing-mill variables involved, the safest procedure when a change is contemplated is to supply the customer with small trial lots and judge the merits of the change on performance alone. This procedure has been followed by our plant and found very satisfactory.

We agree with Dr. Hoyt that a more searching study of impact strength of Bessemer steel at zero and subzero temperatures should be undertaken. Preliminary work of this nature, comparing structural grades of aluminum semi-killed open-hearth and Bessemer steels, showed comparable impact strengths for the two grades. The decrease in impact strength of Bessemer steels was no more severe than for open-hearth steel at the lower temperatures. We realize, however, the need for further investigational work, especially where highly stressed members are concerned.

In our comments on nitrogen content of Bessemer steels, we have made no attempt to correlate the effect of nitrogen on the physical properties, but rather to try to determine the steelmaking variables that directly affect the absorption of nitrogen during blowing. For this reason, we feel that the simpler determination of total nitrogen is just as effective and more direct than the more difficult fractional determination. A more complete understanding of the factors affecting nitrogen absorption is necessary before adequate control of this element can be attempted.

If our efforts have resulted in a stimulation of interest in Bessemer steels, we feel that the purpose of our paper has been partly accomplished.

A Method of Rapid Dephosphorization of Bessemer Steel

BY GORDON M. YOCOM,* MEMBER A.I.M.E.

(Cleveland Meeting, October 1940)

A PROPER consideration of the subject of this paper should include economic aspects as well as the technical phases of the metallurgy, production, and properties of the product.

The metallurgical phases of the processing and properties of the product will be considered only from practical aspects and within the scope of the writer's experience with tonnage production.

The Bessemer process was invented 85 years ago and became important because it put steel manufacture upon a larger and less costly basis. In America the Bessemer production has declined for many years and has not maintained its proportionate place with the rapid advances of the open hearth. The achievements in the open-hearth field were attained by the greater number of technical people attracted to that branch of the industry. The antipathy of technical students for the older and less popular Bessemer field gradually weakened the forces defending it and retarded the development of new and better methods. In Europe the economic advantage of the basic Bessemer process has not been overlooked and the tonnage usually is greater than that of the open hearth. The acid process has been the subject of renewed attention in America during the past few years and those who are more familiar with it are striving to show that the method is too valuable to abandon. A considerable tonnage of Bessemer-blown metal, in both molten and ingot forms, used in connection

with the open-hearth practice makes it an important auxiliary unit to the industry. This practice aids in modifying the price level of heavy remelting scrap in addition to speeding up the open-hearth operation.

The use of Bessemer steel has continued not only because of periodic economic advantages but also because of certain inherent qualities of machinability, weldability and stiffness, which are valuable for many applications. The properties of stiffness and rather high reaction to cold-work require some modification in order to meet the demands of modern methods of processing, which involve cold-reduction and cold-forming. At least one factor contributing to the stiffness of this steel is the relatively high phosphorus content of the acid product. The phosphorus content of the Thomas or basic Bessemer steel of Europe is considerably lower than the normal acid product in America. The American industry has continued the use of the acid process chiefly for the reason that the available ores are more easily adapted to this process from both metallurgical and economic standpoints. In European practice the basic process is necessary with the highly phosphoric ores available and it is sustained to some degree by the sale of the rich phosphate slag as a by-product. The basic process was used in this country at several plants many years ago, but was abandoned for economic reasons.

A part of the past history of these trials is given here because the author believes it has not been published and it has some bearing on the subject of this paper. The information is authentic to the extent that he possesses chemical laboratory notebooks

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* Superintendent, Steel Works and Rolling Mills, Benwood Plant, Wheeling Steel Corporation, Benwood, W. Va.

and blower's data formerly used by relatives and associates who were employed in those plants at the time.

THE BASIC BESSEMER PROCESS IN AMERICA

The European irons for basic operations contained from 1.25 to 1.75 per cent phosphorus and 1.25 to 1.50 per cent manganese, with silicon well under 0.50 per cent. The American attempts to use the Thomas process duplicated these ranges rather closely because it was known that the high phosphorus and manganese contents provided the necessary fuel for attaining the critical temperature for elimination of carbon without the introduction of extraneous fuels. A Bessemer plant at Troy, N. Y., operated from 1895 to 1897 with this kind of iron. The blast furnace operated on two phosphoric ores and two high-manganese ores. The Port Henry phosphoric ore was of the following average analysis: Fe, 60 per cent; Mn, 0.18; P, 1.70; S, 0.030; SiO_2 , 4.0.

This ore was mixed with a Hudson ore of lower phosphorus and higher manganese content. These two ores provided the proper range of phosphorus in the iron but the required manganese content was not entirely obtainable from local materials. Expensive grades of Russian and Japanese high-manganese ores were imported for this purpose. Part of the manganese was obtained by the use of acid converter cinder and ladle slag from the cinder dump of a near-by acid Bessemer plant, but the silica contents of these materials limited their use to a small portion of the burden. The average analysis of the iron used was: Si, 0.45 per cent; S, 0.050; Mn, 1.25; P, 1.25.

A silicon content of well under 0.50 per cent in the iron was desired to prevent major attack of the basic-lined converters, lower limestone consumption and to avoid voluminous slags. The blast-furnace slag was necessarily basic, to keep the

silicon low and the manganese high in the iron. The average analysis was as follows: CaO, 41 per cent; MgO, 9; MnO, 2; FeO, 1.50; SiO_2 , 32.5; Al_2O_3 , 11; P_2O_5 , 0.150; S, 1.75.

The heats were blown down to a low carbon content and after the converter was turned down the slag was scraped off by manual labor. The lime charge was then added in an amount equaling 7 to 10 per cent of the metallic charge, which provided the necessary base to form an oxidizing basic slag for the removal of phosphorus during the afterblow. This slag was removed before the blown metal was poured into the steel ladle, and analyzed as follows: CaO, 43 per cent; FeO, 16.5; MnO, 10.5; MgO, 1.5; SiO_2 , 12.0; P_2O_5 , 16; S, 0.210.

The slag, being rich in phosphorus and lime, was suitable for use as fertilizer, but the agricultural people of that day, in America at least, were not generally familiar with its use or value, and it could not be sold in any great quantity or with any regularity. The Germans were the only customers and at times of high demand purchased it for use abroad.

The company ceased functioning because of the inability to sustain operations by the sale of slag, the high cost of the large amount of manual labor and materials used, the small demand for unfinished steel and its low price during those years.

A Bessemer plant near Pottstown, Pa., practically duplicated the experience of the Troy plant during the same years. This plant continued with the production of rails by abandoning the basic converters and building open-hearth furnaces. We must credit our predecessors for recognizing the need of a lower-phosphorus steel and actually producing it for a short period. The uneconomical methods used in adjusting the local ores to the basic process proved to be too great a handicap. I refer particularly to the methods of obtaining a high manganese and low silicon content. A review of the ore situation of today does

not indicate any important changes favorable to a basic process.

LOW-PHOSPHORUS IRON

The production of low-phosphorus acid Bessemer steel by the use of extremely low-phosphorus ores may be given some consideration. In such a plan there is a scarcity, in the Lake Superior fields, of the very low-phosphorus grades of ore normally used for the production of hematite pig iron for the acid open-hearth process. Ores of 0.015 per cent P or less are shipped by one or two mines only and carry a high premium. An ore of 0.015 per cent P after reduction, with selected coke and limestone of low phosphorus content, may produce an iron of 0.035 to 0.040 per cent P. The loss in weight after conversion in the Bessemer converter may produce a steel of about 0.045 per cent P. A 0.045 per cent P steel would have a wide application but the problem of an economical production of 0.025 per cent P grades on one hand and the normal 0.090 to 0.100 per cent P grade on the other, still exists. In any case this plan tends to destroy a valuable cost differential between Bessemer and basic open-hearth steels and an important economic advantage is lost.

NORMAL-PHOSPHORUS IRON

The available ores are eminently satisfactory and adapted to the present acid process, and they must be utilized. The average analysis of the Bessemer ore shipments for the year 1937 was reported as follows: Fe, 54.66 per cent; P, 0.038; Mn, 0.36; SiO_2 , 8.14.*

The Bessemer iron furnaces usually operate on a mixture of three or four ores and the finished steel has a natural phosphorus content in the range of 0.085 to 0.100 per cent. The utilization of the present Bessemer ores is of first importance. The problem, then, is to develop a low-cost method for dephosphorizing a portion of the ton-

nage in each plant for uses to which the normal grade of steel is not adapted. A method of this kind has been sought by the industry for many years.

LOW-PHOSPHORUS BESSEMER STEEL

We have developed a process operating along these lines at the Benwood plant, and during the past three years about 250,000 tons of low-phosphorus steel has been produced and applied to products where a low phosphorus content is required.

A low-phosphorus steel is required in certain grades because phosphorus is an effective hardener, by solid solution with the ferrite, and reduces the ductility of low-carbon steel. It is generally found that each 0.010 per cent increases the yield point about 700 lb. per sq. in. At about 0.070 per cent P the adverse effect on ductility is so great that a reduction in carbon content is necessary. Tensile strength and elastic limit increase with phosphorus content. Resistance to impact increases up to 0.065 per cent P but above that decreases very rapidly. The effect of oxygen and nitrogen are injurious to certain properties of low-carbon steel, but frequently the bad effects of these elements and improper methods of processing have been attributed to phosphorus. Phosphorus is useful in high-strength steels but harmful in steels when high ductility is required.

Phosphorus is present in iron and steel in the form of Fe_3P and is readily soluble in iron, but practically insoluble in slags. Oxidation is necessary before phosphorus can be removed from iron, and this is more readily accomplished at low than at high temperatures. Above about 2400°F. P_2O_5 is reduced by carbon, silicon and manganese, if present. P_2O_5 is readily soluble in basic slags and practically insoluble in acid slags. The presence of 30 per cent SiO_2 is the upper limit at which a slag will take up P_2O_5 .

In connection with the acid Bessemer process, a dephosphorizing treatment is

* W. A. Haven: *The Manufacture of Pig Iron in America. Blast Furnace and Steel Plant* (April 1940).

best applied to the blown metal, which at this stage contains no silicon and very little carbon. The slag on the metal in the converter at the end of the blowing period contains over 50 per cent SiO_2 . Obviously, this siliceous converter slag must be separated from the blown metal before a dephosphorizing treatment with basic materials is attempted. We have developed an inexpensive method for effecting this separation.

IRON AND SLAG CONTROL FOR DEPHOSPHORIZATION

The physical characteristics of the converter slags of regular practice vary considerably from a very fluid to a very thick and viscous consistency. With such a wide variation in slag condition it may appear feasible to separate the slag and metal by the simple process of reladling. Reladling, however, is not readily applicable in Bessemer plants; most of them were not designed, either in layout or equipment, to handle a reladling operation as a regular routine part of the operation. This is especially true of the older shops where a single hydraulic crane is provided for handling the finished heats from vessel to molds. Expensive additions to existing equipment and the loss of operating time for making such changes for the purpose of reladling are undesirable.

We had noted frequently that a thick, viscous slag was obtained at times, which could be held back in the converter while the blown metal was being poured. Attempts were made to duplicate this type of slag consistently. A study of the slags obtained during the course of regular operations showed, as expected, that the fluidity was affected not only by temperature, the extent of blowing or the percentage of manganese present in the iron, but also by the ratio of silicon to manganese in the iron. Full blowing, side blowing, temperatures in excess of normal and low ratios of silicon to manganese in the iron, all worked singly

or together toward the production of the more fluid type of slag. On the other hand, young blowing and higher ratios of silicon to manganese in the iron produced the desired type of thick slag. The practice of young blowing alone, however, resulted in thin fluid slag with certain casts of iron. Casts containing silicon to manganese ratios of a low order, such as 1 to 1 or 1.5 to 1, require the stopping of the blow some time before the appearance of the first change point, making the method inoperative in so far as the production of very soft steels is concerned.

The suggestion may be made that thick slags could be produced by merely limiting the manganese content to a very low range, perhaps 0.30 to 0.40 per cent Mn. This practice produces satisfactory slags in normal practice. In connection with the dephosphorizing method we have developed, it is necessary to use an iron of high silicon content and a young blowing practice. With such practice an iron very high in silicon and very low in manganese causes the converter lining to build up with kidneys of highly siliceous material in undesirable locations. A change to a medium or full blowing practice would prevent the formation of vessel kidneys but constant changes in blowing practice to suit individual casts of iron introduce undesirable variables in the operation.

The dephosphorizing method we apply requires a blown-metal temperature in excess of normal for the purpose of melting a dephosphorizer added in the cold state. Excess temperatures affect slag fluidity, and we found that a silicon to manganese ratio of 2 to 1 coupled with young blowing was a minimum requirement for the production of the proper kind of thick slag. An iron of $2\frac{1}{2}$ to 1 ratio produced the best type of slag and in addition fits into the ore situation and the ironmaking somewhat better than an iron very low in manganese. Bessemer-iron furnaces are usually operated on three or four ores to produce an

iron of normal phosphorus content at lowest cost. In this case a manganese content of about 0.50 per cent is normal. We preferred to follow this practice but adjust the silicon and manganese contents to the requirements for producing the desired type of converter slag. The control of the silicon to manganese ratio permits the use of a cross section of the available ores rather than of a selected few, and at the same time the proper type of thick converter slag is obtained even with the higher blowing temperatures.

IRON SPECIFICATION FOR DEPHOSPHORIZATION

The silicon content of the iron used in connection with an unmelted dephosphorizing addition required an upward adjustment of about 0.25 per cent above the minimum of 1.00 per cent for normal practice during regular operations. An increase of 0.35 to 0.50 per cent Si is required on starting up turns after the week-end shut-down period. This is in connection with small converters making 6 to 8½ ton heats. Larger vessels should be able to operate with a lower-silicon iron.

A mixture of 40 to 50 per cent direct metal and 50 to 60 per cent cupola metal is charged for each blow; the direct metal analyzes as follows: Si, 1.50 to 1.70 per cent; Mn, 0.60 to 0.65; P, 0.085 to 0.095; S, 0.020 to 0.040. The cupola iron analyzes: Si, 1.15 to 1.25 per cent; Mn, 0.45 to 0.55; P, 0.090 to 0.100; S, 0.055 to 0.065.

This iron is desulphurized as required with soda ash. The cupola charge can be adjusted to produce an iron of high or low silicon content within several hours time, to meet any drastic change in the composition or amount of direct metal. The cupola production can also be adjusted to melt any desired tonnage between 600 and 900 tons per day, and in this manner a further adjustment with the casts of iron can be made by varying the proportion of cupola iron used. The charge to each con-

verter does not vary more than a few points either way from the following specification: Si, 1.40 per cent; Mn, 0.55; ratio, 2.5:1.

During the hot periods in the summer, when the humidity in the air is high, an upward adjustment in silicon and manganese is made, and during the dry cold periods, a downward adjustment.

The blast furnace furnishing the direct metal operates very smoothly as a rule and adjustments of a major character in cupola iron are seldom necessary. The coke is of low sulphur content made up of a mixture of two cokes averaging about 0.75 per cent S. The slag is slightly acid, to meet the requirements for road material, and the average volume is 1000 lb. per ton of iron.

BLOWING PRACTICE

The charge of controlled iron is poured into the converter and after the turning up to start the blow the scrap is added. When making a heat of normal phosphorus content, the average scrap charge is 1500 lb. for the 6½-ton heats. When a dephosphorized heat is being made the scrap charge is reduced 1000 lb., to provide the excess metal temperature for melting the 500 lb. of dephosphorizing mixture. The scrap addition is reduced 600 lb. for a 350-lb. dephosphorizing addition.

The dephosphorized heats are blown young; i.e., turned down from 1 to 6 sec. after the first change appears. When the silicon is in the lower range of the specification, the blow is terminated immediately after the first change because of the more rapid change taking place at this period with low-silicon iron. When the silicon is in the high side of the range, the blow is terminated about 6 sec. after the first change appears, because the higher-silicon iron tends to drag out the change point to a considerable degree. With the average iron of medium silicon content the blow is stopped from 3 to 4 sec. after the first

change point. These slight variations may appear rather small and unimportant, nevertheless they tend to compensate for some of the variations in the iron and result in a more uniform degree of oxidation in the blown metal.

The converter slags are always thick and viscous and analyze as follows: SiO_2 , 63 to 68 per cent; FeO , 12 to 18; MnO , 12 to 18; Fe_2O_3 , 1 to 2; Al_2O_3 , 2 to 3.

The controlled ratio of silicon to manganese in the iron, along with the young blowing practice, produces a slag of uniform composition, with the iron and manganese oxide contents in a desirable range. A lower manganese oxide automatically causes an increase in the iron oxide, and vice versa. The slag remains thick, or heavy, because a proper proportion of acids to bases is maintained. This relation does not vary, owing to the control over the metalloids in the iron from which these oxides are formed.

SEPARATION OF SLAG AND METAL

After the vessel is turned down, a block of wood attached to a long rod is inserted in the nose of the vessel. The block is 4 by 4 in. square and slightly longer than the distance across the nose at a point a few inches above the pouring lip. A light rod is attached to the block at an angle sufficient to allow the slag man to stand far enough to one side to avoid the heat. The only manual labor required is the lifting of the block over to the inside of the nose and dropping it into place. The nose is kept built up to a U-shape at this point, to provide a shoulder for each end of the block to rest against when the vessel is in the pouring position. When the vessel is lowered to pour the blown metal into the ladle the thick slag floats forward against the block, which prevents the slag from entering the steel ladle.

DEPHOSPHORIZATION

A complete separation of slag and metal having been effected in an inexpensive

manner, the dephosphorization proceeds very rapidly and uniformly from heat to heat without delays or interruptions in the cycle. The dephosphorizing material is added to the stream of metal as it is being poured from the converter into the steel ladle. The mixture used consists of: 50 per cent impure lime (Calsifer), 30 per cent roll scale (dried), 20 per cent flux (dried). This mixture is added in the cold state. Such a mixture when melted together to form a slag, analyzes as follows: CaO , 48 per cent; Fe_2O_3 , 28; SiO_2 , 7; Al_2O_3 , 7.

The dry mixture is held in a hopper and runs down a pipe chute directed toward the stream. The rate of flow of the mixture is controlled by a sliding valve at the bottom of the hopper. The flow is adjusted, manually, to coincide with the stream of metal. The blown metal is poured fast, then slow, alternately, to maintain the proper boiling action in the ladle. This reaction should be as vigorous as possible, but the metal should not be permitted to boil up over the ladle. This induces an action that causes a very intimate contact of slag and metal and reduces the phosphorus to the lowest degree. A mild reaction with the slag merely lying on top of the metal as a blanket results in a higher phosphorus content. The addition of the mixture is begun immediately upon the appearance of the manganese boil from the first shovelful of ferromanganese added. The ferromanganese and mixture are added concurrently for a few seconds, the addition of the mixture continues for a few more seconds and is completed when about one-half of the blown metal has left the vessel. The mixture is added just as rapidly as the metal will take it up and melt it and the operation is completed in about 30 sec. The phosphorus is reduced from 0.095, or 0.100 per cent, to 0.020 to 0.040 per cent in that time. The slag is very thin and fluid and has a very low melting point, and after the ladle is filled the reaction subsides to a slight ebullition and by the time the ladle has

reached the pouring platform the slag has risen to the top and the reaction has ceased.

MANGANESE EFFICIENCY

Since the addition of both ferromanganese and dephosphorizer is made to the ladle at the same time, the effect on manganese efficiency may be questioned. It was considered necessary in the first experiments to guard against a waste of ferromanganese and the original mixture contained 10 per cent of high-manganese ore. The heats made with this mixture showed a manganese efficiency above normal and it was attributed at the time to the presence of manganese ore. Gradual reductions in the percentage of manganese ore, however, showed no decrease in manganese efficiency, and the expensive ore addition was eliminated. In our operations the slag is separated from the blown metal in both normal and dephosphorized grades, to obtain the benefit of the higher manganese efficiency. The efficiency obtained in each grade is shown in Table 1.

TABLE 1.—*Manganese Efficiency*

Grade of Steel	Dephosphorized Mixture Used, Lb.	Converter Slag Held Back	Average Mn in Steel, Per Cent	Manganese Efficiency, Per Cent
Regular—normal phosphorus (0.090 to 0.100).....	None	No	0.37	58.3
Regular—normal phosphorus (0.090 to 0.100).....	100	Yes	0.37	65.7
Dephosphorized (0.020 to 0.040 phosphorus)	450	Yes	0.28	69.8

Separation of the converter slag increased the manganese efficiency from 58 to 65 per cent. The dephosphorized steel has a higher efficiency of 70 per cent which probably is due to the higher residual manganese obtained with the hotter younger blow, as compared to the regular steel. The regular steel usually is produced

in a higher manganese range than the low-phosphorus steels, which also lowers the efficiency.

LADLE LININGS

A normal production for each turn of operations consists of about 60 per cent dephosphorized and 40 per cent natural phosphorus grades. There are intervals, however, when 95 per cent of the dephosphorized grades are scheduled continuously for periods of from one to three weeks. The alternate production of the two grades in the same ladle caused a major attack of the ladle lining in regular practice, hence it was necessary to develop one ladle lining for both grades of steel rather than to increase the number of ladles and ladle changes. Experimental runs were made with both basic and neutral materials. These materials were rather high in initial cost and did not stand up long enough to justify the expense. There was some heat loss involved and a tendency to produce ladle skulls. They permitted a reduction in the amount of dephosphorizer required but the over-all costs were increased.

The chrome-brick and monolithic, plastic chrome linings withstood slag and metal attack while at temperatures over 2750°F. However, during the cooling periods between heats the temperature dropped to perhaps 2500°F., and in this range mechanical weakness developed, which caused early failure of the lining. This type of lining produced heavy ladle skulls, owing to heat losses. The extremely fluid basic slag washed out the joint material and there was sufficient heat loss to cause metal to freeze in the open joints with heats of normal temperature. This contributed to failure of the lining because of unsatisfactory joint patches.

The most satisfactory lining developed to date consists of a very hard-burned grade of dense clay brick set up with a thin buttered joint of a chrome-base material containing a vegetable bonding material. Sodium

silicate cannot be used as a bond in this process. The dense, hard brick resists slag penetration, does not spall, and retains some heat. The joint material does not stand up with the brick but there is no tendency to leave skull metal in the joints of an otherwise clean ladle and satisfactory joint patches are obtained. This type of lining normally handles two to four regular heats followed by six to eight dephosphorized heats before being taken out of service for a patch. The ladle reaction of the dephosphorized heats causes an uneven attack of the lining and the thin sections are patched with a rather dry rammed mix of ground ganister and clay. Experiments are being made with a patching mortar made up of several neutral materials and a special binder. This may permit a reduction in the amount of dephosphorizer required for neutralizing acid contamination.

DEPHOSPHORIZING MATERIALS

Many different mixtures of basic materials and fluxes will eliminate some phosphorus from the blown metal if the siliceous converter slag is removed. Generally speaking, those having the best dephosphorizing effect attack the ladle lining to the greatest extent and those having the least effect on the ladle lining usually eliminate the least phosphorus. The most desirable mixture is that which will remove the required amount of phosphorus at the lowest cost for both the mixture and ladle linings. The dephosphorizing materials, being added in the cold state, must be convertible to a slag of low melting point in a very short time after it contacts the hot metal. Lime is the cheapest basic material but in its purer forms has a melting point of 3500°F. or possibly higher. The presence of small amounts of impurities such as silica or iron oxide lower the melting point so that impure lime will frit at 2550°F. or less. The lime base used in our dephosphorizer is of an impure type and compares with a purer lime as shown in Table 2. The Calsifer is brown in color in the calcined

form and is very dense and hard as compared with purer lime. It goes into solution more rapidly than the standard grade of pebble-size chemical lime because of the 4 per cent of natural impurities present. This property is of sufficient value to overbalance the disadvantage of the high silica content. The iron oxide content is a distinct advantage for this process.

TABLE 2.—Comparison of Calsifer and Pure Lime

Impurities	Calsifer (Impure Lime), Per Cent	Pure Chemical Pebble Lime, Per Cent
SiO ₂	1.83	0.36
Fe ₂ O ₃	2.70	0.04
CaO.....	94.36	96.90
MgO.....	0.57	0.95
S.....	0.04	
Ignition loss.....	1.10	1.75

The impure lime will resist slaking to a greater extent than pure pebble lime. The burned rock is crushed to pass through a 3/4-in. mesh screen and very few fines are produced. The small particle size is necessary because of the short duration of the ladle reaction. Larger particles are not completely taken up by the time the ladle is filled. Pebble lime was used for a long period of time but it caused some trouble during certain seasons of the year, owing to dust and fines caused by air-slaking. In addition, cars of fresh material must be on hand and any oversupply must be sacked in waterproof bags and stored in a closed dry place. Dust and fines of lime tend to ball up in the ladle, which reduces the efficiency of the mixture.

FLUXES

The fluxes employed for obtaining the required fluidity of the lime and iron oxide mixture have varying effects on elimination of phosphorus, attack of the ladle lining, melting point, and slag fluidity.

Bauxite produced a slag having some effect on removal of sulphur but the mix-

ture was not entirely satisfactory as a dephosphorizer. Phosphorus was reduced to 0.050 or 0.060 per cent but seldom below that figure. The material contained 53 per cent Al_2O_3 , 15 per cent Fe_2O_3 , 7 per cent SiO_2 , and 22 per cent combined water. The high water content caused a foamy slag, thereby reducing the surface of contact between slag and metal, and less phosphorus was eliminated. The slag caused only minor attack of the ladle lining. An economical reduction in the water content of the crude ore would be required for its use in such a process. Mixtures containing 10 per cent manganese ore and 10 per cent bauxite reduced the phosphorus to 0.040 and 0.043 per cent.

Ilmenite Ore is an excellent substitute for spar. The material used analyzed as follows:

	Per Cent		Per Cent
TiO_2	40	Fe_2O_3	22
SiO_2	3	FeO	27
Al_2O_3	3	MgO and CaO ..	4
Acids.....	46	Bases.....	53

Although TiO_2 is slightly acidic, it is less acid than SiO_2 and in this crude form the bases were 53 per cent and acids 46 per cent, making a practically neutral addition. This material, when used in the same percentage as fluorspar, regularly made heats of 0.030 to 0.035 per cent P. The slag was slightly foamy which reduces its effectiveness but caused only minor attack of the ladle lining.

Soda Ash is an excellent flux for this mixture but when used in the required amounts in the very hot steel the fumes are obnoxious. The slag caused a rather major attack on the ladle linings. Soda ash may be used in the more open type of plant either as all or part of the fluxing addition. It has some added value as a desulphurizer.

Fluorspar produces a slag of excellent fluidity, with no pasty or foamy stage, which provides a maximum amount of surface contact between the slag and metal. After the dephosphorization is completed,

the slag has a very low melting point—between 2000° and 2100°F. The cold slag has the characteristic stoney appearance of heavily sparred slags. The spar is passed through a steam heated drier before the mixture is made up.

The roll scale is selected clean material of small size and is also passed through a drier.

PREPARATION OF THE MIXTURE

The mixture of 50 per cent lime, 30 per cent roll scale and 20 per cent spar is made up in metal containers shortly before using. The ingredients are not mixed in the containers. The lime is on the bottom, the fluorspar is next, and the roll scale is on top. The roll scale is slightly damp at times and contact with the lime is avoided until time for its use. Each container holds 50 lb. of material and any desired weight can be placed in the hopper by dumping the proper number of containers. Attempts to mix the materials in bulk for storage in large bins were not successful. The materials become separated and any dampness present causes slaking of some lime. When the containers are dumped into the feed hoppers next to the vessels a satisfactory mixing is obtained.

LADLE REACTION

The vigorous but controlled reaction in the ladle is a very important feature of the process. At the temperature of molten steel the reactions between slag and metal are almost instantaneous if the slag and metal are brought properly into contact with each other. The action employed in this method is a gaseous stirring promoted by the cold addition to the abnormally hot metal. The use of a molten addition to metal of normal temperature produces a milder and less effective reaction.

Experiments with this mixture added as a molten slag in an equal amount produced 0.040 to 0.050 per cent P steel, when the blown metal was poured into the ladle in the regular manner, as compared to 0.020

to 0.040 per cent P when the cold mixture is used. In order to produce a more vigorous reaction and obtain lower phosphorus, the blown metal must literally be dumped into the ladle in heavy surges, when using the molten material. We found it was less difficult to control the reaction by chemical than by mechanical means.

The use of a cold addition produces a self-regulated ladle reaction obtained automatically with little assistance from the operators. The reaction is the same for every heat and no boilovers occur unless the blown metal is poured too rapidly before the reaction gets well under way.

The gaseous stirring has the effect of bringing the gases dissolved in the steel toward equilibrium and induces a very regular rimming action in the molds. The ingots have excellent rolling quality and a first quality product is obtained with manganese as low as 0.18 per cent in the steel. The beneficial effect of the dephosphorizing treatment on the rolling quality is used to advantage in the regular steel. The regular steel is treated with a 100-lb. addition of the mixture because of its beneficial effect on the rimming action in the molds and the final surface quality.

The degree of phosphorus elimination is proportional to the amount of dephosphorizer used, over and above that which is required to neutralize the acid contamination experienced. The schedule for our conditions is shown in Table 3.

About 100 lb. of dephosphorizer is required to neutralize the acid materials present in our practice and no dependable reduction in phosphorus is effected until 150 lb. is used. The lime, roll scale, blown metal, ladle lining and stopper sleeves all contain acid materials and some contamination from small pieces of converter slag is to be expected.

The heats made for grades III and IV seldom come above the phosphorus specified. When grades I and II are being made an average of 2 per cent of the heats are

diverted to grades III or IV because of their phosphorus content. When grades I or II are being made, 20 to 30 per cent of the heats are 0.020 to 0.030 per cent P. A small number of heats are as low as 0.015 to 0.018 per cent P.

TABLE 3.—*Elimination of Phosphorus*

Grade of Steel	Phosphorus Specified, Maximum	Weight of Dephosphorizer Used per 6½ Ton Heat, Lb.	Pounds per Ton
GY-I	0.035	500	78
GY-II	0.040	450	70
GY-III	0.050	400	62
GY-IV	0.065	350	54

The phosphorus in regular steel may be rather high at times because of changes in coke, ore or furnace conditions. Experimental runs have been made with iron of 0.105 to 0.110 per cent P. In this case, all regular heats were treated with 250 lb. of mix and the ladle tests were usually between 0.085 and 0.090 per cent P, although a few heats were as low as 0.075 per cent.

Experimental runs have also been made for short periods with higher-phosphorus iron. These heats were treated with a maximum addition of mix and the results were as shown in Table 4.

TABLE 4.—*Experimental Runs with High-phosphorus Iron*

Phosphorus in Blown Metal, Per Cent	Phosphorus in Steel, Per Cent	Weight of Dephosphorized Mix Used per 6½ Ton Heat, Lb.	Pounds per Ton
0.147	0.060	500	78
0.150	0.061	500	78
0.188	0.072	500	78
0.192	0.076	500	78

We have reason to believe that greater efficiency of the dephosphorizer may be obtained with larger heats from larger vessels. We have been making a few 8½-ton heats recently and the phosphorus

is reduced from 0.100 to 0.030 per cent with a 500-lb. addition.

LADLE SLAGS

The ladle slags, after dephosphorization, are lower in iron oxide and lime and higher in silica than the usual basic open-hearth slags for low-carbon steel. Apparently the more intimate mixing of slag and metal does not require as high a concentration of essential ingredients in the slag as is necessary for reactions by diffusion. Some slags are particularly high in silica and low in iron oxide but cause no difficulty with phosphorus elimination. The iron oxide content is usually in the range of 9 to 12 per cent, which probably explains the uniform action of the metal in the molds. Aluminum additions to the molds are small in quantity and there is little variation in the amount required from heat to heat. The uniform practice of young blowing, coupled with a correct amount of roll scale in the mix and uniform temperature, makes for an almost automatic control of the degree of oxidation. Typical ladle-slag analyses are shown in Table 5.

variation in the final slag volume. Actually, however, this is not true because varying amounts of slag run off the top of the ladle while the ladle reaction is in progress. The slag should be judged merely on the basis of the available iron oxide present and the amount of phosphorus eliminated. The available iron oxide in the final slag is held to the lowest concentration consistent with satisfactory elimination of phosphorus from the metal. Phosphorus reversion is not a problem because the silica content is always under 25 per cent.

The slag volume in this method represents about 3 per cent of the metal being treated, as against perhaps 10 per cent for basic open-hearth slags, where more impurities are being removed.

HOT-WORKING PROPERTIES

The hot-working and rolling quality of the dephosphorized steel is superior to the untreated normal phosphorus product. The steel is never red-short in the low and medium ranges of manganese. A large tonnage is produced in the 0.18 to 0.25 per cent Mn range but the surface quality is

TABLE 5.—*Typical Ladle-slag Analyses*
PER CENT

Constituent	1	2	3	4	5	6	7	8	9	10
	Heat 17254	Heat 17411	Heat 17413	Heat 18729	Heat 18730	Heat 18075	Heat 3930	Heat 14597	Heat 14598	Heat 14599
CaO.....	36.54	40.48	41.45	52.16	53.50	38.62	44.92	48.42	48.46	51.52
FeO.....	12.29	14.67	11.71	9.52	8.67	12.19	8.76	10.20	12.52	6.94
Fe ₂ O ₃	6.28	9.37	7.32	4.69	4.51	7.01	2.68	3.73	3.66	1.93
SiO ₂	19.25	13.10	13.21	8.07	10.05	24.29	23.66	18.23	17.80	21.30
MnO.....	11.30	8.13	7.23	5.64	5.99	11.71	8.01	7.71	6.08	5.07
P ₂ O ₅	2.66	4.14	4.41	4.19	4.10	4.90	3.81	4.58	5.48	4.82
S.....	0.084	0.115	0.114	0.071	0.100	0.033	0.051	0.165	0.147	0.093
Al ₂ O ₃	3.05	3.06	2.98	3.26	3.61	2.03	2.28	5.99	6.07	6.42
P in steel.....	0.040	0.038	0.040	0.043	0.043	0.021	0.037	0.033	0.023	0.034

The melting points of these slags are from 2000° to 2100°F. In making comparisons of these analyses it should be borne in mind that the weight of lime added in the original mixture is constant. The CaO in the slags, however, varies from 36 to 50 per cent, which indicates a wide

consistently good. The surface condition generally termed as "spongy surface" or "open surface" does not develop even with the hotter heats. The untreated normal-phosphorus steel usually requires a manganese content of 0.40 to 0.45 per cent in order to produce a surface quality com-

parable with that of the low-manganese dephosphorized product. This property is valuable as it permits the application of low-metalloid steel to cold-reduced grades, where a low manganese content has obvious advantages. Skelp of 0.25 per cent Mn and low phosphorus is regularly processed into butt-weld pipe without biting off at the tongs.

The dephosphorized steel ingots are softer than the regular product at normal rolling temperature of 2250°F., and will withstand heavier reductions in the break-down passes without cracking. Blooming-mill tonnage and ingot-to-billet yields were increased with the introduction of the dephosphorized steel.

normal-phosphorus grade the same roll setting will make a 4.030-in. width in the low-phosphorus Bessemer and a 4.060-in. width in the soft open-hearth steel.

PHYSICAL PROPERTIES

Open-hearth vs. Low-phosphorus Bessemer Steel

In order to make a direct comparison of the physical properties of the low-phosphorus Bessemer with open-hearth steel of commercial grade in the black as-rolled condition, sample lots of each were processed under identical conditions. The billets were selected from the same locations in the ingots and rolled to a section $3\frac{1}{8}$ by 0.104 in. thick. The open-hearth was rimmed

TABLE 6.—Comparison of Steels

Blow No. and Grade	Chemical Analyses, Per Cent				Billet No.	Yield Point, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Average Rockwell B Scale
	C	Mn	P	S					
12923 Bes.	0.07	0.41	0.060	0.050	T 2	41,520	58,400	30.0	67.9
					M 4	42,880	56,930	32.0	63.0
					B 6	41,060	55,770	28.0	66.9
					Ave.	41,820	57,033	30.0	66.2
12727 Bes.	0.05	0.27	0.049	0.047	T 2	44,500	53,620	29.0	65.9
					M 4	40,480	42,970	30.0	60.5
					B 6	43,890	57,780	31.0	64.6
					Ave.	42,955	55,127	30.0	63.7
12724 Bes.	0.04	0.26	0.043	0.046	T 2	43,010	53,280	32.0	62.2
					M 4	43,230	57,190	28.0	65.2
					B 6	41,690	54,200	32.0	59.8
					Ave.	42,643	54,890	30.7	62.4
12688 Bes.	0.05	0.28	0.025	0.040	T 2	41,720	54,940	30.0	64.5
					M 4	39,760	51,120	33.0	58.4
					B 6	41,130	52,450	30.5	60.8
					Ave.	40,870	52,836	33.2	61.2
66245 O.H.	0.08	0.41	0.024	0.033	T 2	38,180	53,120	34.0	57.4
					M 4	40,330	52,580	35.0	55.1
					B 6	36,590	51,980	37.0	53.0
					Ave.	38,367	52,560	35.3	55.2

The treated steel rolls and spreads in a manner similar to soft open-hearth steel. With respect to spread in rolling, the low-phosphorus steel lies midway between the regular Bessemer and open-hearth steels. For example, when rolling a skelp section of 4.00-in. width and 0.100-in. thickness of

steel and the low-phosphorus capped and keyed. Bessemer heats of 0.060, 0.050, 0.040, and 0.025 per cent P were selected to show the effect of phosphorus in various ranges (Table 6).

As would be anticipated, the tensile properties and hardness decrease and the

elongation increases with decreasing phosphorus content. Note that the Bessemer steel with the least phosphorus closely approaches the properties of soft open-hearth steel.

Buttweld Pipe.—The routine tensile testing of finished buttweld pipe in the smaller sizes shows a consistent difference between the low-phosphorus and normal-phosphorus grades. The average values for each grade are shown in Table 7.

TABLE 7.—*Buttweld Pipe*

Grade, Per Cent P	Yield Point, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent in 8 In.
0.020-0.040	36,000	55,000	29
0.040-0.055	38,000	58,000	28
0.090-0.100	40,000	62,000	24

The extremely soft grades of pipe made from the 0.020 to 0.040 per cent P steel have a Rockwell hardness of B-40 to B-50. Occasionally low values of B-35 are obtained but usually these samples are of the lower metalloid content with nitrogen values of 0.007 to 0.009 per cent as compared with an 0.012 to 0.014 per cent N usually present.

Cold-reduced Plate.—A comparison of the low-phosphorus Bessemer and open-hearth steel processed in the same manner to cold-reduced strip for galvanized sheets is shown in Table 8.

The dephosphorized Bessemer steel gives a good account of itself when applied to galvanized-sheet products demanding a high standard of flatness and a large and uniform size of spangle, where a drawing quality of forming to drawing standard is satisfactory. All of the available ingot capacity above skelp requirements is so applied. This application averages 10,000 tons per month.

Aging.—Age-hardening has not been a problem with the dephosphorized steel and few data have been accumulated on this subject. Results of age-hardening tests on

one lot of sheets processed as auto body and temper-rolled approximately one per cent were as shown in Table 9.

TABLE 8.—*Steel for Galvanized Sheets*

Grade	Hot Bands		After Cold-rolling	
	Gauge, In.	Rockwell B, Average	Gauge, In.	Rockwell B, Average
Low-phosphorus Bessemer.....	0.072	63	0.015	95
Open-hearth.....	0.072	54	0.015	88

BLACK SHEETS AFTER ANNEALING AT 1230°F.

Grade	Rockwell Hardness	Olsen Value, In.	Elongation, Per Cent in 2 In.
Low-phosphorus Bessemer.....	B-46	0.320	35.0
Open-hearth.....	B-42	0.345	40.0

WELDING AND THREADING QUALITY

In comparisons of machinability of the low-phosphorus Bessemer and other steels, our remarks must be confined to threading qualities. We are not equipped for the production of merchant bar stock, shapes and cold-drawn bars.

As to threading quality of pipe, the every-day practical results indicate that the low-phosphorus steel lies almost parallel with the normal-phosphorus steel and superior to the soft open-hearth product.

The quality of the weld in welded pipe is determined by an inspection of the fracture through the weld after crushing the crop ends. These show a closely knit crystalline grain of practically the same quality as the normal-phosphorus steel whereas open-hearth steel shows a fibrous fracture with less indication of knitting.

The more severe test for determining the quality of the weld in welded tubing is the coiling test. In this method the cold tube is coiled around a mandrel of the specified diameter for the size of tube to be tested.

The low-phosphorus steel tubes withstand this test more satisfactorily than either the normal-phosphorus or open-hearth steel. In addition, the low-phosphorus tubes will coil successfully around mandrels of smaller diameter. Tubes of 1-in. extra heavy pipe (1.315 in. o.d. by 0.181 in. wall), for instance, will coil around a 1 $\frac{3}{4}$ -in. mandrel without breakage of the steel or opening of the weld.

The steel has rather distinct properties of its own and in certain products it is better than either open-hearth or regular Bessemer steel. It has the good welding and machining qualities of normal-phosphorus steel and some of its stiffness and reaction to cold-work, but a much lower degree of brittleness under impact stresses. On the other hand, it has properties of ductility comparable to a low-carbon open-hearth

TABLE 9.—Age-hardening Tests

Analysis, Per Cent				Gauge, In.	
C	Mn	S	P	Hot Band	Cold-reduced
0.05	0.30	0.045	0.045	0.095	0.035

	Original Tests		After 20 Days		Completely Aged	
	Rockwell	Olsen, In.	Rockwell	Olsen, In.	Rockwell	Olsen, In.
	54	0.378	57	0.377	59	0.372
	58	0.369	61	0.347	63	0.341
	53	0.379	56	0.369	60	0.355
Average.....	55	0.375	58	0.364	61	0.356
Increased, Per Cent.....			4.45		10.91	
Reduced, Per Cent.....				2.93		5.07

The low-phosphorus steel gives an excellent account of itself in pipe products for which a soft, ductile material of good welding and threading quality is essential. The products in this classification are ammonia pipe, coiling and bending pipe, electrical conduit, railroad airbrake service, and tubing for oil, gas, and water wells. In electrical conduit the welding and threading quality is superior to an open-hearth steel and the desired low bending stress is obtained. In well tubing the application of sudden shocks is a cause of breakage in high-phosphorus steel and upsetting at the coupling end in open-hearth steel. Since the use of the low-phosphorus Bessemer for this product no complaints involving failures of this type have been received; the steel is stiff enough to prevent upsetting and resists sudden shocks without breakage.

steel of about 0.070 per cent P content but with a better threading and welding quality. It should be applicable to many products in addition to the tubular goods and flat-rolled sheet products for which we have used it.

CONCLUSIONS

The advantages of this method of dephosphorization may be summed up as follows:

1. The controlled ratio of silicon to manganese in the iron: (a) permits the utilization of a cross section of the available Bessemer ores, rather than a few selected ores of higher cost or scarcity; (b) produces an ideal converter slag for slag and metal separation—the crux of the dephosphorization operation; and (c) improves the quality and uniformity of regular steels.

2. The essential ingredients for dephosphorization are provided at lowest cost, and the extra cost of preparing a molten addition is avoided.

3. Quality specifications for the softer grades of steel are met with regularity and uniformity.

4. Both low-phosphorus and normal-phosphorus steels can be made in the same shop at any time with no interruptions in the operation.

5. The advantage of a low-phosphorus steel is obtained, as well as other desirable improvements over the normal-phosphorus product.

6. The extra cost of the method is low and the cost differential between open-hearth and Bessemer steel is not destroyed.

7. The product has a combination of properties of its own that is different from that of the steels made by the usual processes, which makes it valuable for certain applications.

8. Higher ingot-to-billet yields are obtained.

9. The application of the method requires no extensive changes in equipment and can be introduced in a Bessemer plant in a short time with no interruptions in production.

Several disadvantages and limitations of the method have developed, as follows:

1. Lower yields are obtained in the converting mill because of the use of iron of higher metalloid content. The loss in blowing the controlled iron is 9.75 per cent as against about 8.5 per cent for the normal iron of lower metalloid content. Only 3 per

cent of scrap is melted in the converters, as against 7 or 8 per cent for the normal practice.

2. The method is limited to the production of soft steels. Grades of over 0.20 per cent C with 0.75 per cent Mn are difficult to make without introducing a reladling operation.

The degree of success to be attributed to any method for the manufacture of steel should be gauged by the extent to which quality specifications are met, by the control and flexibility in operations, and by the metallurgical and economic aspects of production. We have found that this method attains these objectives satisfactorily and believe it offers a greater future for the Bessemer process.

DISCUSSION

(H. W. Graham presiding)

W. S. SCOTT,* Cleveland, Ohio.—Mr. Yocom's paper covers a most important property of Bessemer steel. The high phosphorus content of Bessemer steel has limited its use for a number of products. The author has not only told us that the phosphorus can be economically controlled but has pointed out the practical problems in connection with this control with a detail and clarity that is remarkable. An avenue for progress has been opened that will no doubt lead to a greater use of Bessemer steel. We now have increased ductility to add to the already well recognized properties of Bessemer steel; weldability, machinability and uniformity.

* Superintendent, Bessemer Plant, Republic Steel Corporation.

Analysis of the Generation and Delivery of the Blast to the Metal in a Bessemer Converter

By J. S. FULTON*

(New York Meeting, February 1941)

THOSE who live in steel-mill towns are so accustomed to the sight of flames spouting from the mouth of a Bessemer vessel that they seldom pause to think of the amazing process behind it. Actually cold air is being blown through a hot liquid and, instead of cooling it, raises the temperature of the liquid. When coffee is too hot to drink, we know that blowing on it will cool it, so it was no wonder that when Henry Bessemer (or William Kelly, as your patriotism chooses) first proposed this cycle of steel production, he was considered mad.

When Bessemer and Kelly started their investigations around 1852, there was not much practical knowledge of metallurgy and, in consequence, there was wide variation in the product made by their process. It was appreciated that the silicon, carbon and iron were all potential fuels, but not until Mushet discovered the beneficial effects of having manganese in the pig iron did the process really become commercial.

Bessemer's patent of 1855 covered a crucibleful of liquid iron into which a refractory tuyere was lowered and the blow started. Since that time virtually every conceivable form of vessel, bottom arrangement, tuyere size and location have been suggested or tried. There have been stationary vessels with fixed bottoms, that were side, top or bottom blown; tilting vessels with two sets of side tuyeres at different elevations; vessels like a three-compartment septic tank; vessels of a cylindrical

form supported on the long axis with tuyeres along the side submerged by a partial rotation of the vessel (this type continues in copper refineries); portable vessels to make the blow in a ladle over a mold in a foundry; a combination of a cupola and converter in one shell, and various other arrangements. But in all these experiments, compressed air for the blast was presupposed and there was little discussion of the quantity or quality of the air delivered to the tuyeres.

At one time or another various practices that now are forgotten have been tried or suggested: for instance, the use of inert gas at the end of the blow; the addition of fuel to the blast; the use of hot-blast stoves; the drying of the air to a minimum moisture in the blast. Except in the last-named method little attention was paid to the quality or quantity of the air blown.

PHASES

Of the many papers published on various phases of the Bessemer process, nearly 170 according to one bibliography, over 90 per cent were concerned with the metallurgical phase and less than 10 per cent discussed various sections of the pneumatic phase. Since the two phases are coincidental, apparently nine times as much thought has been given to the result as has been given to one of the causes of the Bessemer process.

Is it not possible that if more attention had been paid to the pneumatics so many papers would not have had to be written on the troubles in the metallurgical phase? A study of published papers and conversation

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with "old timers" shows little change in blowing practices for many years. The use of centrifugal blowers with their different delivery characteristics has had slight effect on specified blast pressure. As in the past, the operator on the pulpit is "pressure conscious" and watches this and the "flame" and alters the "pressure" on the vessel as experience dictates. The pressure-flame relation are his criterion and little attention has been paid to the thermal, frictional and velocity losses between the blowing engine and the entrance to the tuyeres. It is obvious that any decrease in pressure or volume will decrease blowing costs if the time is not extended.

The discussion in this paper will be confined to the pneumatic phase, as any improvement in that phase will lower the blowing cost, improve bottom life and help to improve the quality of product.

When a Bessemer vessel is being blown the blast of air performs at the same time two different functions, both of which are necessary for successful production of steel. The first function is mechanical or pneumatic, in that the air is transported by the energy of the blowing engine to the exit of the tuyeres from which it expands at high velocity into the liquid iron, with consequent agitation. At this point the thermal and metallurgical phase commences, from the combination of the transported oxygen with the fuels, silicon, manganese, carbon and iron. Obviously there should be some certain relation between the pneumatic and metallurgical phases, but up to the present time little attention has been given to the potential benefits of this ideal balance between oxygen supplied and fuel burned.

Basically the Bessemer process consists of burning its fuel in minimum time, but with more emphasis on production of steel than on the generation of blast.

The typical tilting vessel is egg-shaped, with removable bottom tuyeres and wind box. Through one of the trunnions support-

ing the vessel, air is piped to the wind box. From there it escapes into the metal, ending its pneumatic phase and starting the metallurgical phase. The products of combustion escape through the mouth of the vessel, together with a certain amount of entrained or exploded solids.

CAPACITIES OF VESSELS

Unfortunately, there is no accepted method of rating the capacity of a vessel, as there is for a blast furnace. For illustration, a particular shell size may be rated as 25 tons. While it is usual to rate this as 25 long tons of steel produced per blow, some plants might use this value as the weight of iron charged, while others use either value in terms of short tons. There are other variations also:

1. The vessel may have from 27 to 35 tuyere blocks per bottom, with a new length of 26 to 36 in. The tuyere block usually has seven $\frac{5}{8}$ -in. holes, though some have 10 to 13 $\frac{1}{2}$ -in. holes.
2. The blast pressure before the control valve at the pulpit may range from 18 to 33 lb., average around 30 lb., only a few plants knowing the true pressure in the wind box.
3. The temperature of the blast in the wind box may be anywhere from 60° to 350°F., depending upon the atmospheric temperature, the blast pressure, and the length and exposure of the blast line.
4. The centrifugal blowers serving four of these 25-ton vessels may have capacities of: 32,000 cu. ft. per min. at 26 lb. blast pressure; 40,000 cu. ft. per min. (30 lb.) (two vessels); and 65,000 cu. ft. per min. (35 lb.) to serve lap heats on two vessels 3500 ft. from the blower. The fourth is served by reciprocating blowing engines and is blown at 60 r.p.m. for an expected capacity of 40,000 cu. ft. per min. at about 30 lb. blast pressure.

In only one case is a permanent record kept of the volume blown. To further complicate this picture of blowing capacity, one

20-ton vessel has been blown continuously with blower capacity of only 18,000 cu. ft. per min. at 20 lb. before the pulpit, where 30,000 cu. ft. per min. at 30 lb. is used on the same vessel at another plant. The answer to this seeming contradiction is that the first plant blows a heat about twice as long.

5. The percentage of silicon, manganese and carbon is a variable, as is the temperature of the pig iron as it enters the vessel. While it is possible to develop, in advance of the blow, the weight of fuel to be consumed and to notify the pulpit operator, the writer knows of no plant where such practice is followed. Why would not this knowledge be a help to the operator in determining his blowing practice, particularly if at the same time he had a visible indication of the actual amount of air leaving the blower?

6. The heat may be blown as short a time as 5 min. or as long as 25, depending upon the tuyere area, the analysis of the iron, its temperature, and the desired quality of the blown metal.

Because of all these variables, it is impossible for the superintendents of two plants to make an intelligent comparison of their blowing practices. Although blast-furnace men have a measure of comparison based on 50 cu. ft. of air per pound of coke, and for equivalent furnaces and burdens they show about the same blast pressure, it would be unheard of for two Bessemer men to discuss a comparable relation between wind and fuel, and as for blast pressure, they never have enough. The Bessemer operators have no logical basis for comparing operations.

Can it be that the furnace men are fuel conscious because their operating costs are penalized by excessive use of fuel, and the Bessemer men are not because their fuel is "free"? Is it not possible that if the Bessemer operator knew the exact weight of "fuel" he must burn, and had an adequate knowledge of the pounds of oxygen per minute he was pushing through the bath,

he could avoid the surplus heat at the end of the blow and so make a better product more economically?

REASONS FOR LACK OF IMPROVEMENT IN BESSEMER PROCESS

There are two very plausible answers for the lack of improvement in the Bessemer process in the past 20 years. In spite of them, one company has improved its product by using an "electric eye" to indicate the end of the blow, but no one has made a complete study of the pneumatics to see whether costs and quality could be improved by changes in the conduit and the furnishing of instruments to the pulpit operator. The first reason is that there has been a feeling for years that the Bessemer process was dying. The attitude is to leave well enough alone, inasmuch as the necessary money is not available for improvement. The second reason is that everybody has felt that while horsepower could be saved by reducing the blast pressure and volume blown, it was nevertheless necessary to maintain a minimum blast pressure at the pulpit in order to keep the metal out of the tuyeres.

What would be the use in saving blowing power if the decreased pressure allowed the metal to drop through the tuyeres into and through the wind box? An operator from a plant trained on 30-lb. pulpit pressure would be afraid to turn his vessel up with only 20-lb. pressure, while the 20-lb. operator would be afraid that he might blow all of his charge out of the vessel if he turned it up against 30-lb. blast. Both of them overlook the fact that these five values—blast volume, blast pressure, blast temperature, tuyere area, time of blow—are more closely related than the Dionne quintuplets.

BLAST PRESSURE

In the firm belief that the Bessemer practice, far from dying, is coming back to life, we will concentrate on the second attitude, as part of the pneumatics.

Most operators have been trained in reciprocating blown plants and are taught to watch the blast pressure, because of the unrecognized delivery characteristics of a

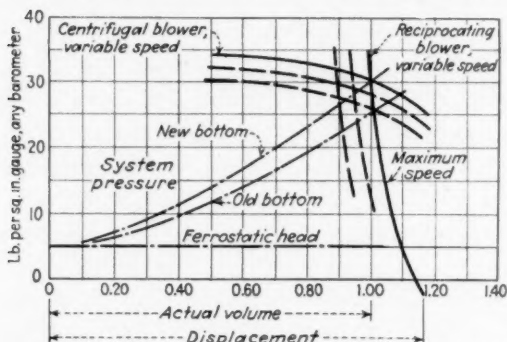


FIG. 1.—COMPARATIVE DELIVERIES, CENTRIFUGAL AND RECIPROCATING BLOWERS.

reciprocating compressor or blower, or "blowing tub," as it is called in this application.

It is customary to think of a "blowing tub" as a generator of blast pressure, but this is not true. The blowing tub inhales and exhales a certain weight of air per minute at a particular speed, and it transports this weight of air into the discharge or blast line. The pressure necessary to push this weight of air per minute through the discharge orifice (tuyeres) is the discharge pressure at the blower, after the velocity and friction heads of the blast line have been added. While the compressor falls off very little in volumetric efficiency for an increased blast pressure, it cannot transport an appreciably greater weight of air (cu. ft. per min.) with a lowered discharge pressure (Fig. 1).

As the tuyere shortens in service, there is less tuyere friction and so more weight of air can be pushed through. But since the blowing tub cannot transport more air at the same speed, the usual practice is to operate it at a higher speed and pressure, so that even shortened tuyeres can be filled. However, one providential thing happens that no one considers. At the same time that the tuyeres shorten, it is also necessary to blank some from erosion or leakage, and

this results in balance between air supply and demand: Wind-box pressure new \times tuyere area full = wind box pressure old \times tuyere area (full — blanks).

Fig. 1 shows both the undesirable delivery characteristic of the reciprocating unit and the more desirable one of the centrifugal blower, which gives a greater volume of air against a lower blast pressure.

For an increase in volume of 10 per cent, the blowing tub could deliver only against 5-lb. gauge pressure instead of 30-lb. gauge. The centrifugal blower would drop only from 30 to 28-lb. gauge.

On Fig. 2 are plotted the cubic feet per min. intake at 14.4 lb. abs. and 26°F. and blast pressure for each heat on a particular bottom served by a centrifugal blower. Neither the volume nor the pressure is constant during any blow; 35 lb. was the maximum pressure needed for 1771, the fifth heat, while only 29 lb. was needed for 1783, the last heat recorded, for the same nominal production. The rapid-motion chart from which this was prepared is shown in Fig. 3. This chart records the volume and blast pressure at the blower without showing any change in the state of the air between the blower and pulpit from blast-like radiation, or drop in pressure from friction, or loss of volume from leakage.

The usual plant shows about 0.5 lb. friction between the blower and the pulpit and a loss of temperature of about 50°F., from 279° to 229°F. Then each cubic foot leaving the blower would become:

$$1 \times \frac{25.0 + 14.4 \text{ lb. abs.}}{24.5 + 14.4} \times \frac{460 + 229}{460 + 279} = 0.943 \text{ cu. ft.}$$

at the pulpit. At one plant the equivalent length of 36-in. blast line is 5200 ft. but only 1.0 lb. pressure is lost, though the temperature dropped 200°F. in an atmosphere of 26°F.:

$$1 \times \frac{25.0 + 14.4}{24.0 + 14.4} \times \frac{460 + 69}{460 + 279} = 0.735 \text{ cu. ft.}$$

the putalpit.

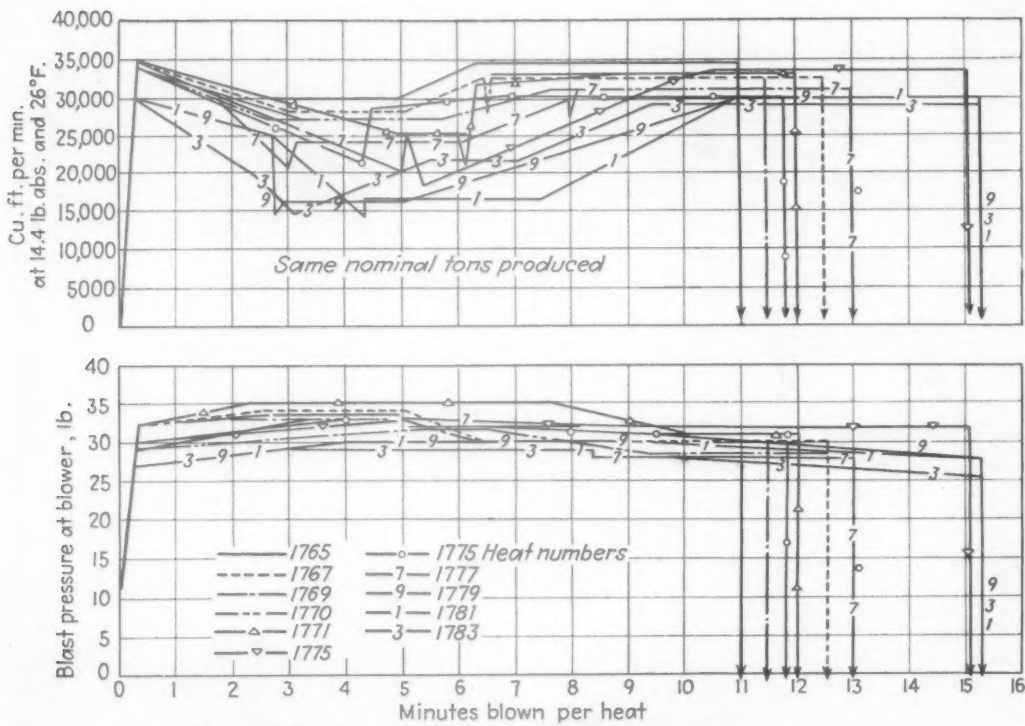


FIG. 2.—HEATS ON BOTTOM SERVED BY CENTRIFUGAL BLOWER.

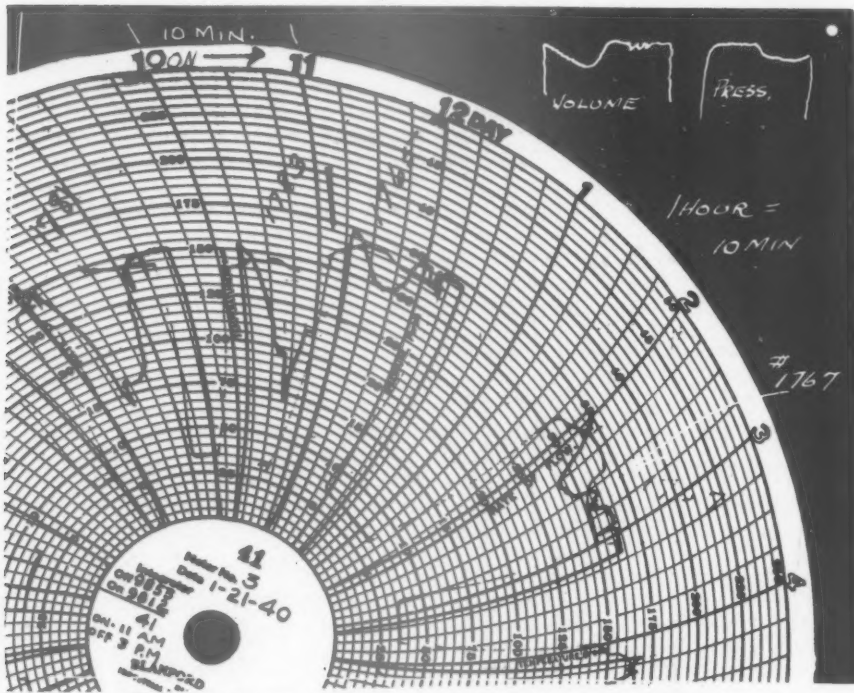


FIG. 3.—RAPID-MOTION CHART USED IN PLOTTING FIG. 2.

The flow through the tuyeres would vary inversely as the $\sqrt{\text{density}}$, which at the second plant is $\sqrt{\frac{0.950}{0.735}} = 1.135$ and would

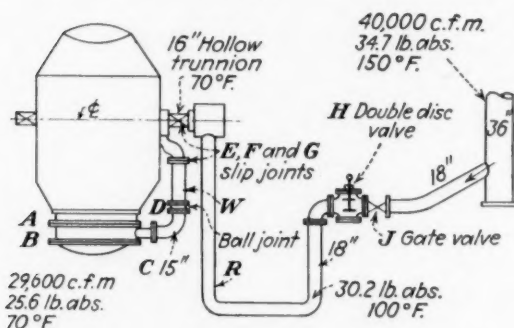


FIG. 4.—TYPICAL ARRANGEMENT OF 25-TON PLANT.

Test at 40,000 cu. ft. per min., 60°F., 14.4 lb. abs., cold bottom.

Pressure before $J = 34.7$ lb. abs. and after H wide open 30.2 = 4.5 lb. loss.

Pressure in wind box = 25.6 lb. abs., = 4.6 lb. loss.

Total loss from 36-in. main into wind box = 9.1 lb.

Peripheral length of joints, A, B, C, D, E, F and $G = 78$ ft.

There were 192 $\frac{3}{4}$ -in. holes in 32 tuyeres during test. Each $\frac{3}{4}$ -in. hole at $C = 1.00$ could carry 200 cu. ft. per min. but previous test of individual tuyere block, $C = 0.74$, 40,000 cu. ft. per min. $\times 0.74 = 29,600$ cu. ft. per min. through 32 tuyeres, or 10,400 cu. ft. per min. lost between main and tuyere entrances.

Feet per Second Velocity

In main = 46.3

18-in. pipe = 212.0

Trunnion, 16-in. = 269.0

Wind pipe, 15-in. = 307.0

Wind box, 8×2 ft. = 5.5

Into $\frac{3}{4}$ -in. tuyere = 715.0; 29,600 cu. ft. per min.

No correction for leakage except at tuyeres.

require 13.5 per cent more blowing power and would deliver 13.5 per cent more oxygen and nitrogen to the bath. If they were both blown the same time, the latter should blow hotter and require more steam or scrap.

It is the writer's understanding that the vessels, nominally 25 long tons of steel, at South Works and Gary of Carnegie Illinois Steel, McKeesport of National Tube and Aliquippa and South Side of Jones and Laughlin, are the same except for their

bottoms. These have from 27 to 35 tuyere blocks with seven $\frac{5}{8}$ -in. holes.

A study of one of these plants indicates the probable friction losses of all, from a point before the control valve at the pulpit to the entrance of the tuyeres in the wind box. We will study one as though 40,000 cu. ft. per min. of atmospheric air were delivered to the pulpit at 20-lb. gauge and 150°F. The particular vessel was calibrated, in that the air was metered to it, alone, and the leakage was determined at the various joints from the riser connection to the hollow trunnion down to the wind box and from the various joints between the cover, wind box, bottom and vessel.

The arrangement of one of the 25-ton plants is shown in Fig. 4, with the results of this calibration test on a cold bottom, giving the observed pressures and temperatures at several points. The pressure losses and indicated leakage are startling, but they are substantiated by a similar test at another plant.

While the velocities are extravagantly high in the air lines, it must be remembered that all of these vessels are operating at a considerably higher rating than when purchased. There is no doubt that considerable blowing power would be saved if the various joints were improved to decrease leakage, if some other form of control valve giving less turbulence were used, and if the conduits were streamlined to avoid both high velocity and continued changes in velocity head.

SUGGESTED IMPROVEMENTS

Several plants are making an investigation in this direction and it will be interesting to note some of the suggested improvements:

1. Instead of the ball joint at D between the wind pipe W and the wind-box ell C , a loose piece is provided that can slide across C 's flange to accommodate angular displacement of W . At least one plant has this in service.

2. Instead of a slip joint at *E*, it is proposed to make *W* a corrugated expansion joint, lined outside and inside by a cylindrical steel shell.

3. It is also proposed to make a similar flexible connection between the riser pipe and the housing around the end of the hollow trunnion. At present, as the trunnion journal wears down, there is no means of maintaining an airtight joint around the trunnion extension.

4. It is proposed to use either a tight butterfly valve or a plug valve in place of the double-seated disk control valve at the pulpit.

5. While the velocity through the hollow trunnion is high, its short length will not cause a great loss. However, when new saddles are ordered it would be advisable to make the "trunnion hole" equal to the size of the supply pipe if it can be done without too great a change to the stand or other part of the equipment. It is interesting to note that three nominal 20-ton vessels having a normal blow of 25,000 cu. ft. per min. at 30 lb. at the pulpit have trunnion holes of 20.5-in. diameter instead of the 16-in. on these 25-ton vessels.

6. The ordinary cover plate on the wind box is a dished plate of steel, approximately $\frac{3}{8}$ in. thick. At 20-lb. wind-box pressure and 8-ft. diameter, there is a load on it of 145,000 lb. This distorts the cover and opens the joint around the rim. The flange should be stiffened, the bolts moved closer in, more bolts used, and the cover stiffened. Studies are being made at different plants on the simplification of the assembly of the bottom to the vessel and the increased tightness of the joints. In order to assure the proper alignment of flanges, one plant proposes to use guide studs. Several different methods of tightening the joints are suggested but so far they are all on paper.

7. After the air is delivered into the wind box, half the volume may be considered as passing across the box, hence the 5.5 ft. per sec. shown on Fig. 4. In order that the

29,600 cu. ft. per min. may pass through the 192 $\frac{3}{4}$ -in. tuyere holes, it is necessary that it be accelerated to the 715 ft. per sec. velocity in its vena contracta. It may be considered that the flow conditions are either at CP_1 where *C* is coefficient of capacity, in this case 0.74, or full P_1 is working on *C* area of hole.

With 192 holes fighting for the air, it is logical to assume that with only a single point of supply to the wind box not all can obtain the same amount at all times. Undoubtedly there is a continued "tug of war" between the holes. (Remember that each hole is potentially capable of running with a high *C* but the fact that 192 holes are open does not mean that each delivers the same quantity of air.) It is the writer's belief that the usual failure of certain tuyeres after a given number of heats is attributable to this "tug of war." On another vessel tested "hot" the *C* was as low as 0.67, indicating either excessive turbulence within the wind box or a tendency of the outer ring of holes in each tuyere to rob the inner ones—or possibly a still greater leakage.

In order to provide better distribution, the writer has suggested running two bustle pipes around the wind-box periphery, one furnishing air to the outer ring of tuyeres and the other to the middle of the bottom. It is also suggested that if a funnel could be attached around the wind-box end of each tuyere there would be easier acceleration to the holes. If the inside diameter of this cup were 7 in., its velocity would be

$$\frac{29,600 \text{ cu. ft. per min.}}{60 \times 32} \times \frac{14.4 \times 4}{7 \times 7 \times \pi} = 58 \text{ ft. per sec.}$$

This 58 ft. per sec. would be in the direction of the flow into the tuyere holes, rather than the 5.5 ft. per sec. across the entrance.

8. In order to show the influence of the temperature of the air entering the tuyeres upon the amount of air that will be handled for the same wind-box pressure, Fig. 5 has been plotted. The curve for 70°F. was plotted from page 114 of the 1940 edition

of the Compressed Air Data Book. The curves for 140°F. and 210°F. were developed from the fundamental flow formulas. These curves are for nozzle flow, and while

The curves for 70°F. were drawn for both atmospheric back pressure and for a back pressure of 5-lb. gauge to cover the 15 lb. ferrostatic head and 1 lb. assumed for the

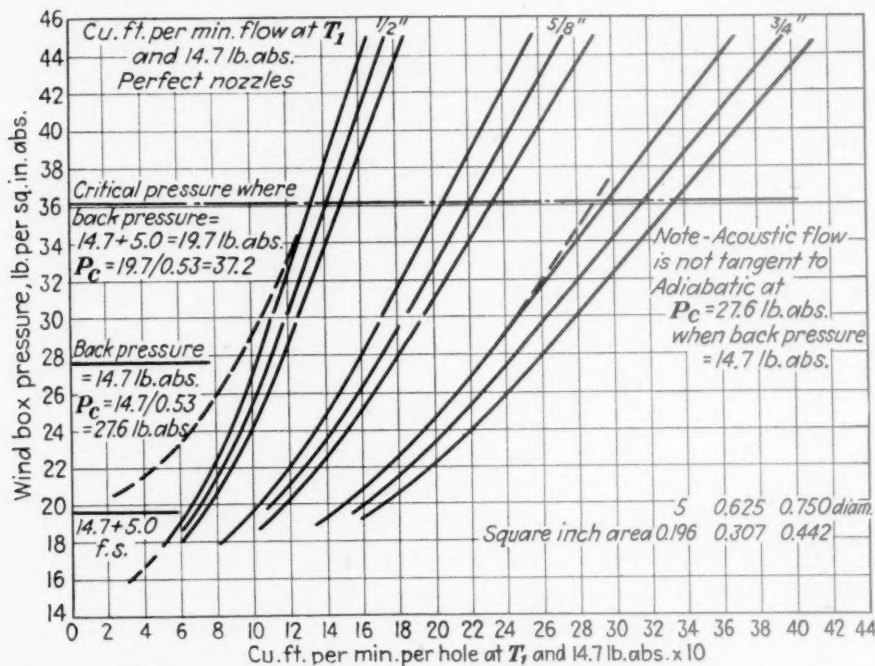


FIG. 5.—CURVES FOR NOZZLE FLOW PLOTTED FROM COMPRESSED AIR DATA BOOK.

the tuyere is not a perfect nozzle the curves at least illustrate the influence of temperature.

Where the back pressure on the nozzle is greater than 53 per cent of the initial pressure, i.e., $BP > 0.53P_1$, the flow is in the adiabatic range. The formula for this is on page 367 of the Compressed Air Data Book.

Where the back pressure on the nozzle is less than 53 per cent of the initial pressure, i.e., $BP < 0.53P_1$, the flow is in the critical or acoustic range. The formula is:

$$\text{Pounds per second} = \frac{0.5303 \text{ area in sq. in. } CP_1}{\sqrt{T_1}}$$

where C = nozzle coefficient,

P = absolute pounds pressure on entrance of nozzle,

T = absolute degs. F. on entrance of nozzle.

pressure necessary to get the products of combustion through the nose of a vessel. Because of the great length of the tuyere as compared to a perfect nozzle, there will be an unknown amount of friction, H_f . Consequently, the formula must be modified to read:

$$\text{Pounds per second} = \frac{0.5303 AC(P_1 - H_f)}{\sqrt{T}}$$

where P_1 = wind-box pressure.

Of course friction must be included, but the writer has been unable to find any formula applicable to the extremely high velocities and rough surfaces in the tuyere. Even if a formula were developed it would be applicable for only one particular length and flow. Since both are changing as the heats progress, there would be little benefit from such a formula.

Fig. 5 shows that at 36 lb. abs. the perfect 5/8-in. nozzle would handle:

204 cu. ft. per min. at 70°F. flowing temperature,

217 cu. ft. per min. at 140°F. flowing temperature,

230 cu. ft. per min. at 210°F. flowing temperature.

At 210°F. there would be:

$$\frac{(460 + 70)(230)}{(460 + 210)(204)} = 0.89, \text{ or } 89 \text{ per cent as much oxygen and nitrogen, but } \frac{(230 \times 100)}{204} - 100 = 12.5 \text{ per cent more}$$

volume for agitation at the same upstream pressure.

If there were surplus oxygen at 70°F. but just enough at 210°F., from Fig. 5 the blast pressure could be dropped to 32 lb. abs. for atmospheric discharge, or a saving of approximately 7 per cent of the blowing power.

Both the flows are in the acoustic range for atmospheric back pressure and so do not exactly apply to the flow through a tuyere, unless

$$\frac{14.7 + 5.0 + 1.0}{P_1 - H_f} = 0.53$$

but even if the flow dropped back into the adiabatic range, there is still a potential saving from increased wind-box air temperature.

9. The writer believes not only that the blast line should be insulated but that there are further possible savings from hot blast. The objection is made that this would raise the bath temperature, but this 140° rise gives 11 per cent less oxygen for combustion. The flame temperature possibly would be higher but less heat would be generated, assuming that the decrease of 11 per cent O₂ still left sufficient oxygen to burn out the silicon, manganese and carbon in the proper time.

Having shown this pneumatic advantage from hot blast, let us leave it to the metallurgists to prove it is wrong.

10. Since a cubic foot of air saturated with water vapor carries more oxygen and

less nitrogen, why would not the Bessemer process be helped by adding moisture in the blast line to the equivalent of 10, 20 or even 30 grains of water per cubic foot at atmosphere and also making up any deficiency of heat from dissociating H₂O by using hot blast.

TEMPERATURE OF BLAST

Can the air pick up any heat in passing through a bottom in blast? The end of the tuyere in contact with the metal may reach a temperature of 2600° to 2800°F., and there is a rough conduit to cause turbulence, which improves the convection from the walls. Two things must be considered: (1) the tuyere material is a poor conductor of heat; (2) during the time available with a 36-in. tuyere and an average velocity of 750 ft. per sec. the air would be in the tuyere only $\frac{1}{250}$ sec. As a generality, the tuyere in blast uses up 12 to 15 lb. pressure in its length to furnish some friction and a very large velocity head. If this energy were expended in a work expansion, the exit temperature T_2 would be lower than T_1 , but from the tuyere form and rough surface it is probable that the T_2 approximates T_1 . At the tuyere entrance there might be a submergence in temperature at the vena contracta but probably this is dissipated by whirls and eddies and the friction in the following length.

There is continued debate as to the movement of the metal bath, the majority holding the view that the metal moves up the center of the vessel, returns down the sides and then passes back to the center to start a new cycle. The writer believes that the jets of air leaving the outer ring of tuyeres around 1200 ft. per sec. erect a pneumatic picket fence that certainly interferes with any liquid flow across them, and that these jets would also induce an upward movement between the tuyere blocks in this ring. That would leave the central portion working on much the same batch of metal all the time, which could be accom-

panied by a higher temperature, as the outer layers would be cooled by radiation.

PROBLEMS

Why should not there be more area in the vessel just above the tuyeres, and lanes be

up recording gauge. The heavy outer line, the pressure, on Fig. 6 was due to an undampened light spring, since a reciprocating blowing tub was operating in parallel with a centrifugal blower. As seen on this and on Fig. 7 with a dampened stiffer

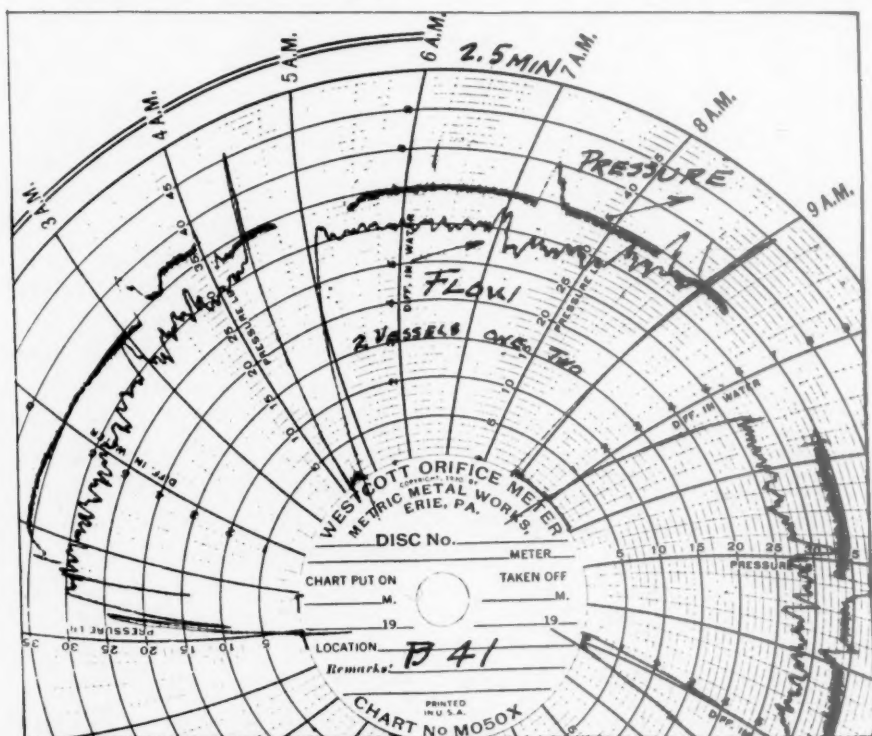


FIG. 6.—CHART OBTAINED ON SPEEDED-UP RECORDING GAUGE IN CALIBRATION OF A VESSEL IN SERVICE.

left by respacing tuyere blocks, so that the metal would have a chance to get back to the center?

Why does the bottom usually retreat faster in the center, although most damaged tuyeres that have to be plugged are in the outer ring?

Does the tuyere burn off from the blowtorch action of the combustion reflecting back from the dome of liquid above the tuyere, or does it spall off from alternate heating and cooling?

In the calibration of a vessel in service, by means of an orifice well located in the riser pipe to the hollow trunnion, the charts in Figs. 6 and 7 were obtained on a speeded-

spring, the head pressure on the orifice was virtually constant, but at different levels when one and two vessels were in blast. The inner line in each is the differential across the orifice. The swings in volume are on about a 20-sec. cycle.

The pressure and air volume have been plotted on Figs. 8 and 9, where the changes in volume are more noticeable, as is the difference in blast pressure for single-vessel and two-vessel blowing off of a common blast line.

Since the air was blown through a charged vessel, there should be no change in ferrostatic head on the tuyeres, therefore the air left the tuyere at $14.6 + 5.0$ lb.

ferrostatic head, plus whatever was needed to force it out of the nose of the vessel.

Since the blast pressure was constant within 0.5 lb., how can the volume change by the 10 per cent shown on these charts?

From the fundamental flow formula for a

lower flow above this pressure. Apparently $300 - 27.6 = 3.4$ lb. is the tuyere friction at this pressure.

Two later tests were run on an empty vessel, one with 168 tuyeres 34 in. long and the other after 31 heats had reduced the

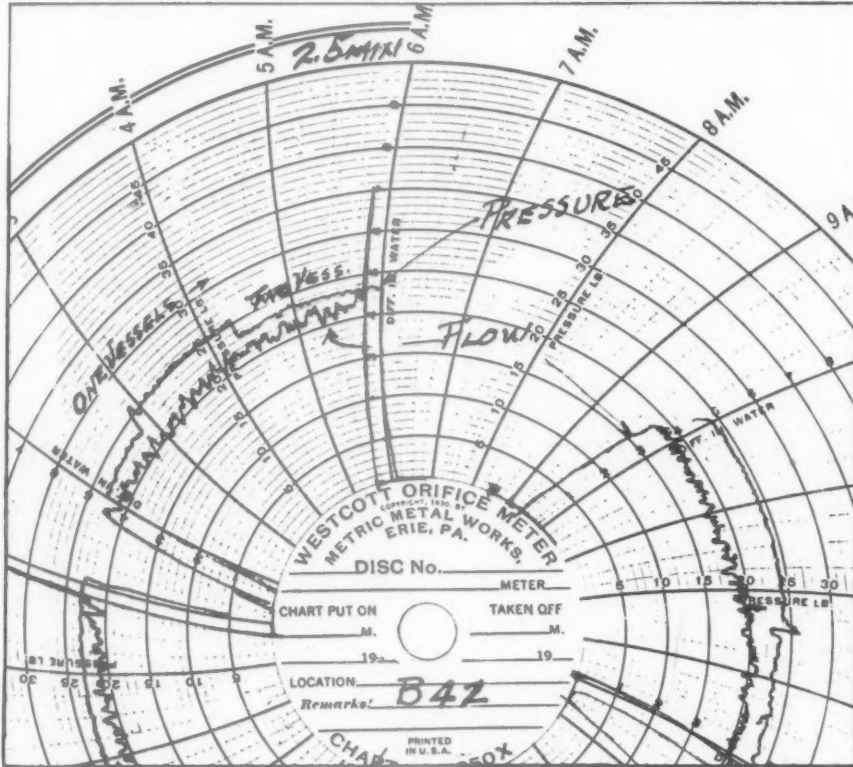


FIG. 7.—CHART OBTAINED ON SPEEDED-UP RECORDING GAUGE IN CALIBRATION OF A VESSEL IN SERVICE.

perfect tuyere, the volume of air cannot change when P_1 , T_1 , and BP_1 are constant, yet it did change. Undoubtedly the great ratio of length to hole diameter removes the tuyere from the class of a nozzle and brings the flow into a range that has not received much study.

A previous test of a cold bottom with atmospheric discharge is plotted in Fig. 10, where a distinct break was found in the type of flow around 31.0 lb. wind-box pressure. Where the perfect nozzle flows were plotted on Fig. 5, it was noted that the adiabatic flow was tangent to the acoustic at the critical pressure of $14.7/0.53 = 27.6$ lb. abs., but turned back and indicated a

length of the tuyeres and caused six to be blanked with 126 holes 10 to 12 in. long. These three tests were with tuyeres having seven $\frac{5}{8}$ -in. holes.

On Fig. 11 are plotted these three tests and also the laboratory test of a single tuyere block 36 in. long having ten $\frac{1}{2}$ -in. holes.

Unfortunately, while a break is shown in all the flow curves, it is not clearly limited as to the upper and lower limits of the pressures. However, the 175-hole test showed this break as being between 31.0 and 33.0 lb. abs. for 14.6 plus 0.5 back pressure. Assuming that the friction remains at 3.4 lb., this break can be projected into the

range of the test of the vessel in service shown in Figs. 6 and 7. Then

$$15.1 \text{ lb. BP}/(31.0 - 3.4) = 0.55$$

$$15.1 \text{ lb. BP}/(33.0 - 3.4) = 0.51$$

and both are almost in the range of critical

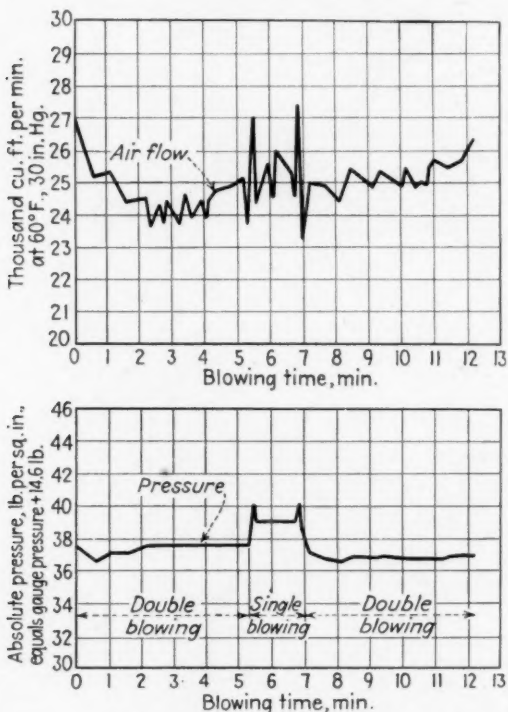


FIG. 8.—CONVERTER RECORD, ONE TUYERE BLANKED.
6:15 a.m. to 6:27 a.m., Aug. 10, 1940.

flow. Assuming that the charged vessel has a back pressure of 14.6 plus 5.0 ferrostatic head plus 1.0 = 20.6, the wind-box pressure, neglecting tuyere friction, would be $20.6/0.53$ average = 38.9 lb. abs.; or, including friction 42.3 lb. abs. from Fig. 7, the flows were erratic at either 41.0 or 39.0.

This is not a particularly close check, but indicates that the irregularity is not caused by the churning of the bath.

The writer has been unable to find any explanation for this irregularity that can be demonstrated mathematically, but believes that in some way the irregularity is aggravated by the number of holes and by the length of the tuyere. Fig. 11 shows the least distortion of the flow curves for the $\frac{1}{2}$ -in.

laboratory test and the $\frac{5}{8}$ -in. 126-ft. hole assembled-bottom test.

It also shows that there is less distortion on the $\frac{5}{8}$ -in. test with tuyeres 10 to 12 in. long than when they were 34 in. long. If this irregular flow is substantiated by other tests,

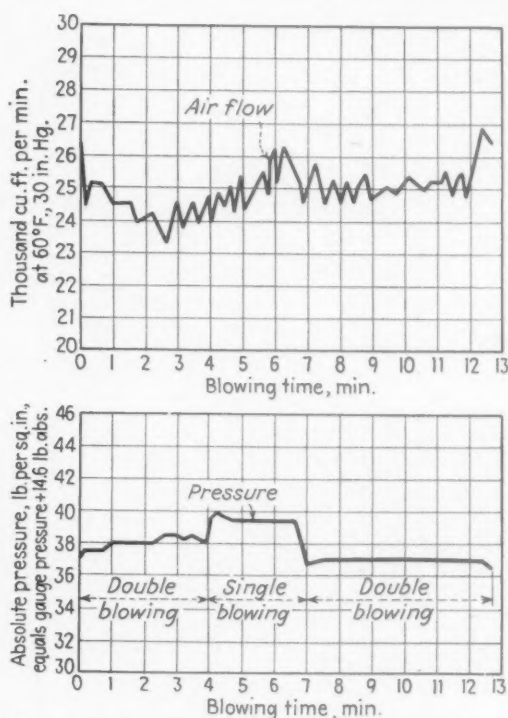


FIG. 9.—CONVERTER RECORD, FIVE TUYERES BLANKED.
12:10 p.m. to 12:22 p.m., Aug. 10, 1940.

the writer suggests that the bottom life might be increased either by using less tuyere area at a higher pressure to throw the flow into the acoustic range above the 0.53 point, or more tuyere area at a lower pressure to throw the flow into the adiabatic range below this 0.53 point.

STALAGMITES

It is characteristic of Bessemer blows that the blast pressure begins rising and the volume decreases a few minutes after the blow starts. After a few minutes, as shown by heat 1765 on Fig. 2, the volume rises and the pressure drops to normal till the blow is finished. As the bottom wears down (heats 1779, 1781 and 1783) the sag in volume is

continued longer and the total blowing time is lengthened.

The customary explanation for this is the formation of slag and the greater viscosity of the bath during this period. This is a good explanation but is not convincing

Co., confirms this growth. At Ensley some heats are blown as short a time as 4 min., which does not create sufficient heat to melt the stalagmites. Consequently, after every heat of this sort, "high pots," it is necessary to knock off the stalagmites with a hose, as

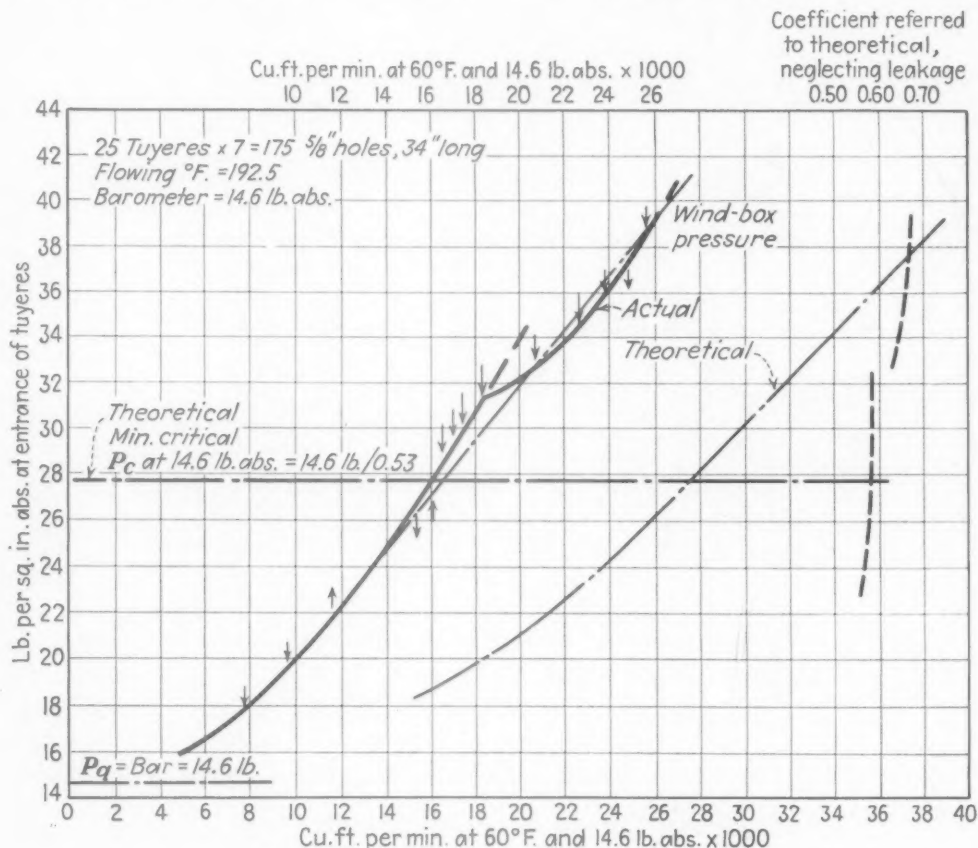


FIG. 10.—"COLD" CALIBRATION OF BOTTOM.

because of facts Mr. Sam Cresswell, Bessemer Superintendent, South Works, Carnegie-Illinois, discovered several years ago. He found that during this period a stalagmite forms around and over the end of each exit tuyere hole, which consists of a mixture of iron and carbon having a higher melting point than the temperature of the bath at that time. As the blow continues these stalagmites are gradually melted off and so are not apparent when the bottom is examined after pouring. Mr. Alan Lowman, Bessemer Superintendent at Ensley plant, Tennessee Copper, Iron and Railroad

otherwise the bottom would be closed in less than 10 heats. Perhaps when the stalagmites break or melt off they take a piece of the tuyere with them.

While Mr. Leek, Chief Engineer of Wokington Iron and Steel Co., was in this country last year, he told the writer that hot metal at his plant was at such a low temperature that unusually high silicon was specified. The blows for the same grade of steel require more than twice the time used in the United States. At one time he tried 36-lb. pressure at the pulpit without materially shortening the time of blow.

Whether the cause is silica slag or stalagmites, or a combination of the two, it is apparent from Fig. 2 that the vessel will

necessary to carry 33.5-lb. gauge at all times, with an obvious loss of energy as compared to a single vessel served by a

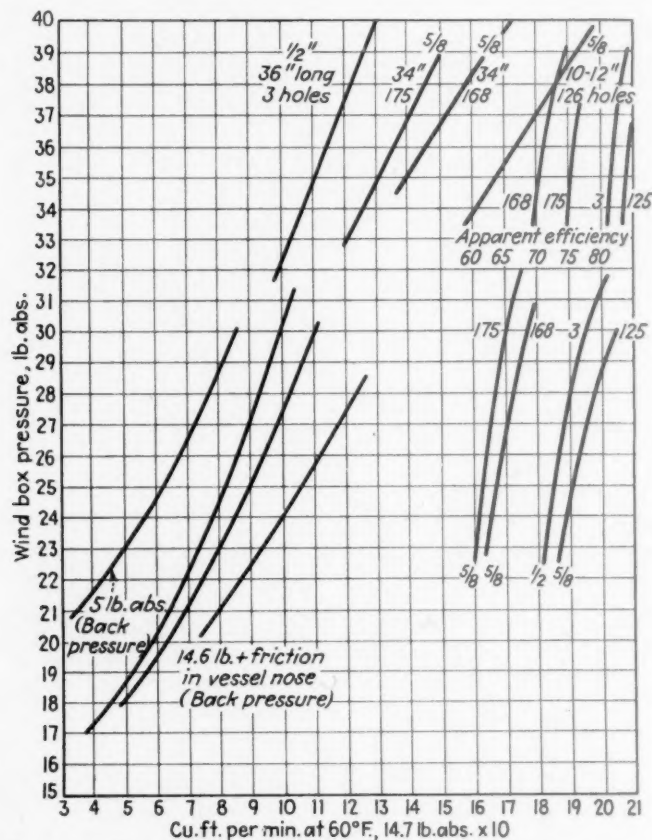


FIG. 11.—FLOW THROUGH SINGLE TUYERE HOLE OF SIZE SHOWN.

take neither constant volume nor constant pressure. The operator should be provided with means to change the volume and the pressure quickly (for they are pneumatic Siamese twins) in accordance with his wishes.

Fig. 2 shows also the folly of operating two vessels at once on the same blast line, unless both bottoms are in exactly the same condition. To show the momentary variations in volume and pressure, assume that heat 1783 is turned up after heat 1765 has been in blast 3 min. The comparative volumes and pressures are plotted in Table 1.

Since the system must be prepared to accept the vessels, as turned up, it would be

single blower. What happens to a system is shown on Figs. 8 and 9.

TABLE 1.—Comparative Volumes and Pressures as Bottom Ages

Time		Blast Pressure, Lb.			Volume, 1000 Cu. Ft. per Min.		
Hr.	Min.	Heat 1765	Heat 1783	Difference	Heat 1765	Heat 1783	Total
	3.0	33.5	27.0	6.5	30.0	30.0	60.0
1	4.0	33.5	27.5	6.0	30.0	26.5	56.5
2	5.0	33.5	28.0	5.5	30.0	23.5	53.5
3	6.5	32.5	29.0	3.5	34.5	14.5	49.0
5	8.0	31.5	29.0	2.5	34.5	20.0	54.5
7	10.0	30.5	29.0	1.0	34.5	21.5	56.0
8	11.0	30.0	29.0	1.0	34.5	21.5	56.0
10	13.0	(1767)	27.5		(1767)	28.5	28.5
12.5	15.5	32.5	26.0	6.5	35.0	28.5	63.5

MAINTENANCE OF FULL BLAST PRESSURE

Another phase of the pneumatics is worthy of study—the maintenance of full

submergence of 6-lb. gauge, of which 5 lb. is from the bath and 1 lb. from the pressure needed to push the gases out of the vessel.

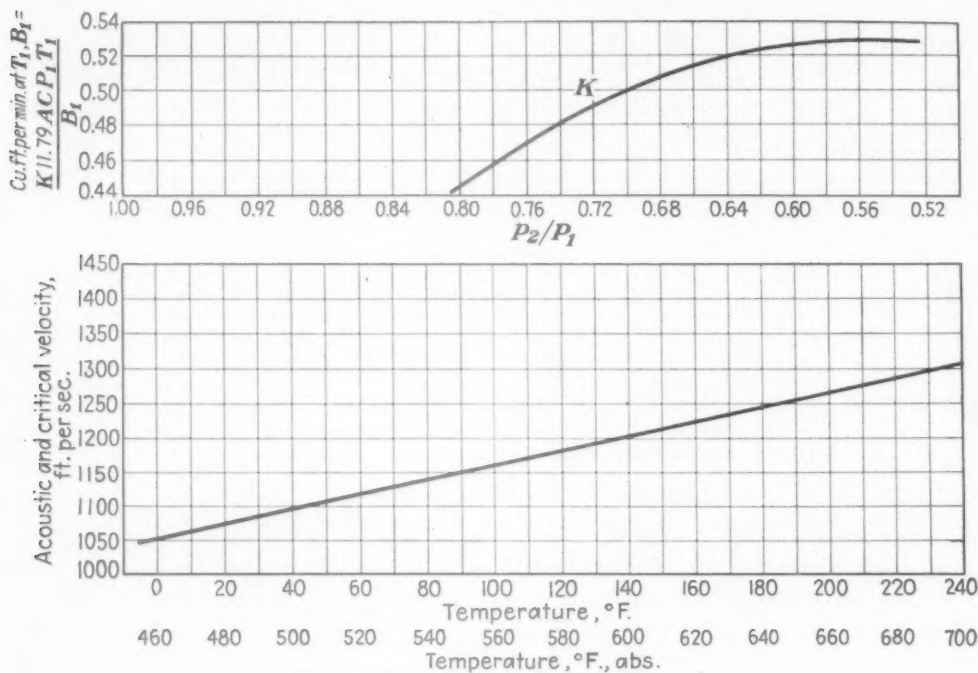


FIG. 12.—FLOW IN ADIABATIC RANGE.

blast pressure in turning up or turning down the vessel.

Starting with the vessel on its side, its angular rotation upward results in the tuyeres being gradually covered with the metal of the bath. To simplify study of the flow of air through the uncovered and covered tuyeres and all of the various submergences, consider only two tuyeres, one on the "belly" side and the other diametrically opposite on the "top" or "back" side. When the vessel is turned up to a point where the top tuyere is just above the level of the bath, an angular turn of about 45° , the gravity ferrostatic head on the bottom tuyere is nearly the same as when the vessel is vertical, because of the particular shape of the lining just above the bottom. Erosion of the lining should decrease the submergence at any angle of rotation.

The bottom tuyere would then have a

With wind-box pressure of 20-lb. gauge the ratio of pressures would be

$$\frac{14.4 + 6.0}{14.4 + (20.0 - H_f)} = 0.593 \text{ where } H_f = 0$$

Assume the $H_f = 3.0$ lb. friction.

$$\text{Then } \frac{20.4}{14.4 + (20.0 - 3.0)} = 0.65.$$

From Fig. 12, the "quantity of flow factor" K has a value of 0.52, which is in the adiabatic velocity range.

The ratio of pressures on the open tuyere would be

$$\frac{14.4 + 1.0}{14.4 + (20.0 - 3.0)} = 0.49$$

so the flow would be acoustic and the value of K would be 0.53, but the quantity flowing out would be at 31.4 lb. abs. $\times 0.53 = 16.65$ lb. abs. BP . Therefore, the relative flows would be:

$$\frac{0.53 \times 16.65}{14.6} \div 0.52 = 1.14 \text{ or } 14 \text{ per}$$

cent more air would flow through the open tuyere neglecting friction. The friction would be $3.0 \times (1.14)^2 = 3.9$ lb. This would decrease the outlet flow to $30.5 \times$

is both side and bottom blown, and the continuing chemical combinations must be allowed for in starting the "turn down."

It would not be very difficult to provide

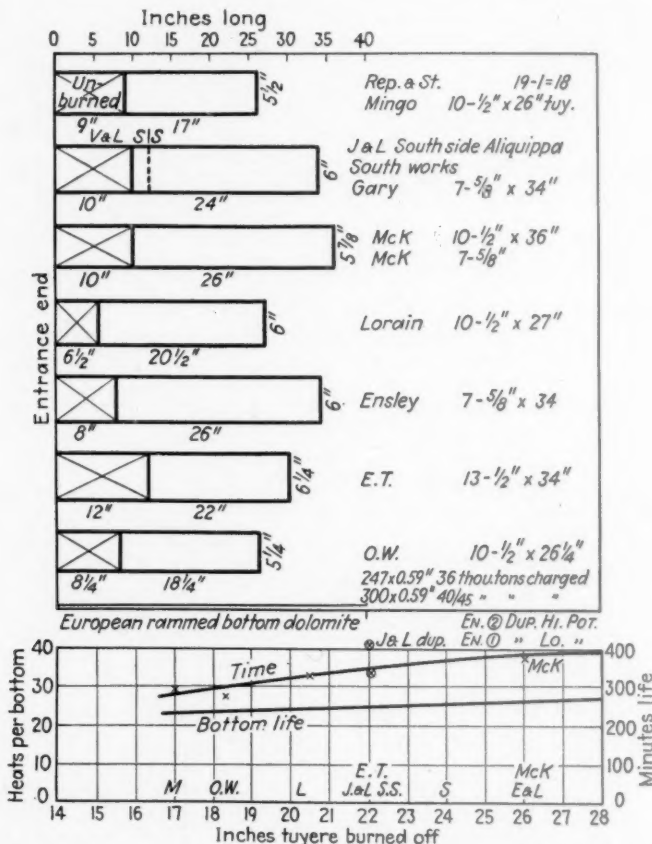


FIG. 13.—AMOUNT OF TUYERE BURNED OFF PER HEAT PER MINUTES BLOWN, FOR FULL BESSEMER STEEL.

$0.53 = 16.15$ lb. abs. and so decrease the excess flow to 12.5 per cent. Perhaps if the relative flow for the covered and uncovered tuyeres were calculated for each angle of rotation, some angle might be found where this value would be exceeded, but owing to the short time this condition existed, coupled with the receiver volume of the blast line, no different flow would be noticed at the blower.

While the rotation of the vessel shows so little change to the pneumatics, there might be some benefit to the metallurgy if the blast were gradually cut off as the vessel turned down. During this period the vessel

for this automatically by a rearrangement of the wind box and hollow trunnion.

The first step to be taken would be the casting of the wind box with a partition between the "belly" and "back" sections, and provided an air connection to the bustle pipes of each section.

The second thing to be done is the furnishing of a new saddle casting carrying the hollow trunnion with two air outlets.

The third step would be to build a distributor on or in the hollow trunnion, so that the angular upward rotation of the vessel would open the port to the "belly" section and then the port to the "back"

section of the wind box. Depending upon the proportions of the vessel, the "belly" would be wide open at 40° and the back at 80° above the horizontal. In turning down the sequence would be reversed. While desirable, it would not be necessary for the distributor or the wind-box partition to be absolutely tight.

Since this method of controlling the air to the two sections of the bottom is automatic, there would be no more danger of dropping the metal through the tuyeres than at present, and a benefit might be gained for the metallurgical phase.

Most vessels are now blown with tuyeres having seven $\frac{5}{8}$ -in. holes. Since there is reason to believe that lower pressures cannot be used in the wind box, if the operator can be sure the blowing equipment will give quick response to his change in demand, investigations should be made with larger tuyere holes. One plant found that the use of $\frac{3}{4}$ -in. holes allowed the pulp pressure to be dropped from 29 to 23-lb. gauge when six $\frac{3}{4}$ -in. holes were used instead of seven $\frac{5}{8}$ -in. holes. However, the heats were "sloppy" because the full number of tuyeres was used. The bottom life was less on account of tuyere breakthrough. It was difficult to keep the metal from dropping back through the tuyeres.

If six $\frac{3}{4}$ -in. holes gave too thin a wall in a tuyere block of 6-in. diameter, is there any reason why the block should not be 7 in. or even 8 in. if thereby the bottom life would be extended?

If the larger holes were used, the total number of tuyeres could be decreased to give the same square inches of area and decrease the friction.

From Fig. 13 the only reasonably consistent thing found around the Bessemer plants is the inches of tuyere burned off per heat for full Bessemer steel and per minutes blown. Both Ensley and McKeesport burn off 26 in. of the tuyere before the bottom is changed and Mingo 17 in. If there is anything in proportion, the first two should

only have to "make bottom" $1\frac{1}{2}$ as often as Mingo. However, McKeesport and Mingo both average 23 heats per bottom with 390 and 290 min. life, respectively. Ensley blowing more duplex steel blows as many as 470 min. It is the writer's opinion that the greatly increased life at Ensley, leaving out any consideration of bottom materials or assembly practice, is due to the lower temperature at which the duplex blows are poured.

The European basic vessels have gone to 40-in. rammed bottoms. Is there any reason why we should not consider a new bottom with $\frac{3}{4}$ -in. or even 1-in. holes in tuyeres 48 in. long?

RECOMMENDATIONS

The writer recommends that:

1. The air circuit be streamlined and the joints around the vessel be made shipshape.
2. The blast lines be insulated.
3. Hot-blast stoves or heat exchangers be installed to raise the blast temperature in the wind box.
4. The humidity of the blast be maintained at a uniform level either by: (a) refrigeration, or, preferably, (b) injection of moisture to a controlled level, if for no other reason in order to decrease the nitrogen.
5. The operator be advised of these corrections in items 3 and 4 or have control of them.
6. Each vessel be calibrated to determine the combination of wind-box pressure, tuyere combination, tuyere size that will give the optimum combination of blowing cost and bottom life.
7. The operator be provided with visible indications of the amount of wind entering the riser pipe even on two vessels on a common blast line, and if possible the wind-box pressure as a check on leakage.
8. The operator be provided with all the instruments that can improve the product without making the operation too complex and that he be provided with a decent place

in which to work in comfort. Could he not look at the "flame" from an easy chair with push buttons, and with instruments on a table before him for control of the process?

9. The Bessemer fraternity get together and really do something about the many pneumatic things unknown about, or wrong with, this process.

ACKNOWLEDGMENTS

The writer wishes to express his thanks to the friends who have given information that has made this paper possible.

DISCUSSION

(C. D. King *presiding*)

D. R. LOUGHREY,* Pittsburgh, Pa.—It is gratifying to everyone interested in the manufacture of steel to note the increasing return of interest in the Bessemer process in the past few years. Probably the most spectacular, dramatic and remunerative manufacturing process ever to be developed, whose products were good enough to carry our fastest trains and build our biggest bridges, this process has continued to slip toward oblivion, principally because, by its very nature, it has been technically hard to control. Like a wild horse, whose value lies in its terrific speed, it has been allowed to run free, almost to its death, because the scientific cowboys have been too slow to rope it and put the harness on.

Fortunately, science has been catching up with this problem before it is too late and seems to be in a position now to apply instruments that are sufficiently sensitive and rapid to match the reactions of the process. This able and timely paper by Mr. Fulton will open many avenues of thought long since forgotten by the operating men and never seriously considered by the research engineers, yet it is one of the most important phases of the process. The facts that he uncovers and the questions he asks should awaken the operating and research people to the realization that an inefficient and possibly destructive condition exists in the pneumatic assembly of our Bessemer plants, which should be remedied at once. Let us con-

sider some of the problems which arise in attempting to do this.

The Bessemer process is valuable because of its speed. High speed, properly controlled, spells success today more than it ever did before. Why then, we ask, should the most rapid method of steelmaking ever devised be abandoned with scarcely a move to preserve it? Would it not seem more logical to subject each phase—layout, construction, raw materials, pneumatic system, metallurgy, control instruments and operating technique—to the most exhaustive scrutiny and experimentation by a competent force of research engineers? This has been done on processes that did not offer nearly so much hope for reward.

A Bessemer converter is a rather permanent structure. Unlike the open-hearth furnace, its "lines" cannot be changed with every rebuild. Its body is made up of cast or form-rolled sections, while the bottoms, tuyere plates, etc., require costly patterns. Blast-producing equipment is the most expensive and permanent of all. Because of this expense and permanency, management has been reluctant to specify or accept anything of an unproved or insecure nature and, by the same token, equipment manufacturers cannot sell, nor can they afford to guarantee, installations that depart radically from accepted standards. Any experimenting with equipment changes, aside from being expensive in themselves, usually entail serious delays to operations and a consequent penalty in production or quality.

Mr. Fulton points out that we introduce our blast into a long pipe line where it loses head because of friction and also a large portion of its initial temperature. We then force it through a double disk or balanced type valve where we lose about 3 lb. pressure, thence through a constricted hollow trunnion at a speed of 750 ft. per sec. into a wide wind box where the speed is reduced to 5 or 6 ft. per sec. Then, in a final display of pneumatic ignorance, we shoot it through some 200 small tuyere holes with the speed of a rifle bullet, 1200 ft. per sec. All this we do through an antiquated series of joints and connections which leak blast and reduce bottom life. Because of Mr. Fulton's constructive criticism while he was obtaining material for his paper, several companies have already begun to redesign and modernize their pneumatic systems.

* Jones and Laughlin Steel Corporation.

Operating men have long forgotten, if they ever knew, the amount of oxygen actually necessary to complete the reaction of blowing a heat. Aside from adjusting the blast pressure in small amounts to regulate temperature, they have been blast conscious only to the extent of keeping tuyeres from burning on the one hand and keeping the metal in the vessel on the other. If 20 lb. pressure would blow a heat in 15 min. and 25 lb. would do it in 12 min., they have demanded and generally received the 25 lb. Some of them have been surprised recently to find that actually they had less than 15 lb. in their wind boxes.

Large excesses of oxygen passing through molten iron cannot help but affect the metallurgy of the process to a marked degree, especially when it carries with it about four times its own weight of that latest bugaboo of the steelmaker, nitrogen. Obviously it behooves every operator and metallurgist to find out how much air and what kind of air we need; to find out where the happy medium between production speed and metallurgical expediency lies, or even if there is such a thing.

Why not experiment with different arrange-

ments of the tuyere blocks or the size and number of the holes in them? Why not try two bustle pipes and place funnels at the base of the tuyeres? Mr. Fulton asks these questions, and rightfully, because there is a definite need for improvement. The metallurgists and testing engineers ask other questions, and money has been spent lavishly in less fruitful branches of the steelmaking art to find the answers to just such things as these.

It is to be hoped that somebody may shortly find it possible to make available a small experimental converter where the many problems confronting us may be solved practically and at a reasonable cost. A large proportion of the experimental work in improving any manufacturing process is expended in giving it more productive speed. The Bessemer process has had this speed for many years and it is the opinion of many people that if the scientific brains of the steel industry could be induced to converge upon this process to anywhere near the extent that they have done on other processes, the lights of Bessemer converters would dot more skies than ever before and the industry would profit exceedingly by it.

Influence of Chemical Composition on the Hot-working Properties and Surface Characteristics of Killed Steels

By GILBERT SOLER,* MEMBER A.I.M.E.

(New York Meeting, February 1940)

PRODUCERS of alloy steels recognize the importance of chemical composition in relation to the hot-working properties and the typical surface defects found in their product. Each analysis of steel has its own peculiar characteristics. Under conditions of standard mill practice each analysis is susceptible to certain types of defects. Mill practice must be varied to obtain the best combination of surface and internal quality in the product.

Chemical composition influences the cast structure and crystallization characteristics of the ingot. It also determines the rate of heating and cooling, the plastic hot-working range, and the phase structure of the steel at various temperatures, as well as the tendency toward scale formation and decarburization. This paper endeavors to emphasize the manner in which chemical composition affects the various properties of steel, and to indicate the relative importance of these factors in relation to the hot-working properties and surface characteristics of killed steel. The influence of chemical composition may be outlined as follows:

- I. Effect on the cast structure of steel, including:
 - A. State of deoxidation, and type of inclusions.
 - B. Gas content of steel.
 - C. Freezing point and melting point of steel.

- D. Crystallization characteristics and segregation.

- II. Effect on the hot-working properties and surface characteristics of steel, including:

- A. Plastic hot-working range.
 - B. Phase structures at hot-working temperatures.
 - C. Rate of heating.
 - D. Cooling characteristics.
 - E. Scale formation.
 - F. Surface decarburization.

EFFECT OF CHEMICAL COMPOSITION ON CAST STRUCTURE OF STEEL

State of Deoxidation and Type of Inclusions.—The state of deoxidation is limited by the final chemical analysis desired in the finished product, and is controlled primarily by carbon, manganese, silicon, and aluminum, and to a lesser degree by chromium, titanium, vanadium, or other deoxidizing elements. The degree of deoxidation affects the density of the cast structure and broadly classifies the steel as killed, semikilled, or rimming. This in turn manifests itself in surface characteristics.

The manner and extent of deoxidation also controls the amount, type, and distribution of nonmetallic inclusions formed. The equilibrium of manganese, silicon and aluminum with the slags and pouring refractories with which the metal comes in contact is important, especially in regard to inclusions of fire-clay origin. Some surface seams and hot-working difficulties can be traced to nonmetallic inclusions.

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Fig. 1 shows a general seamy condition, with some scabs and checks, on a bloom of S.A.E. 10105 steel. Fig. 2 illustrates the effect of excessive nonmetallic inclusions on

carbon monoxide gas on the structure of rimmed ingots is well known.

Freezing Point (Liquidus) and Melting Point (Solidus) of Steel.—The "freezing



FIG. 1.—BLOOM SURFACE OF S.A.E. 10105 STEEL, SHOWING GENERAL SEAMY CONDITION.

the hot-working properties of 5 per cent Cr-Mo steel with titanium. In the piercing operation ruptures and seams were formed on the inside of the tube. Figs. 3 and 4 show the structure in transverse and longitudinal section. Many nonmetallic inclusions can be seen.

Gas Content of Steel.—Gases may have an indirect effect on the hot-working properties of steel by modifying the forces of crystallization and segregation in the ingot. Also, they may directly affect the surface to a small degree. The solubility of hydrogen is increased by the presence of certain elements. Steels with high chromium or silicon contents absorb hydrogen readily.

Nitrogen may be absorbed by steel. Its presence as a nitride in high-chromium steels refines the grain size of the cast structure and increases the gamma field in the solid state. The effect of evolution of

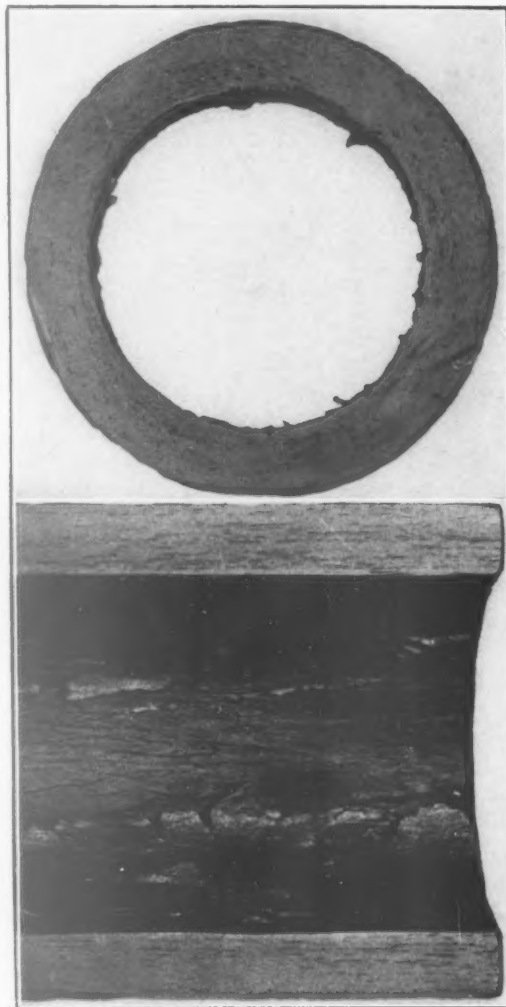


FIG. 2.—RUPTURES AND SEAMS ON INSIDE SURFACE OF PIERCED TUBE DUE TO NON-METALLIC INCLUSIONS.

5 per cent Cr-Mo steel with titanium.

point"* of steel is controlled to a large extent by the carbon content and to a lesser degree by other alloying elements.

* The term "freezing point" is used herein to designate the temperature of the liquidus at which freezing begins on cooling, or melting ends on heating. The term "melting point" is used herein to designate the temperature of the solidus at which melting begins on heating, or freezing ends on cooling.

Steels of high carbon content will have a relatively low "freezing point," consequently the amount of superheat above the solidification range can be greater than in low-carbon steels with similar slags and melting facilities. The degree of superheat

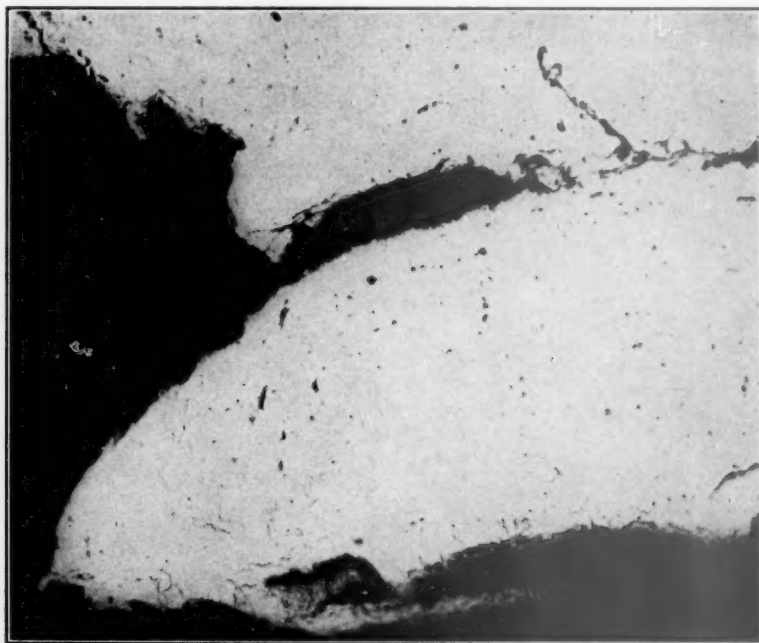


FIG. 3.—NONMETALLIC INCLUSIONS. $\times 75$. TRANSVERSE SECTION OF RUPTURED TUBE SHOWN IN FIG. 2.



FIG. 4.—NONMETALLIC INCLUSIONS. $\times 100$. LONGITUDINAL SECTION OF RUPTURED TUBE SHOWN IN FIG. 2.

above the "freezing point" may affect ultimate crystallization and segregation.

Phosphorus, titanium and silicon lower the "freezing point" to some degree but the effect is negligible, as these elements usually are not present in large amounts. Chro-

shows the presence of flute cracks in a bloom of S.A.E. 2315 steel that has been reduced from a round duodecagonal big-end-up ingot. Note that these cracks are



FIG. 5.—SCABBY BLOOM SURFACE.

mium, when present in large amounts, as in the stainless steels (12 to 18 per cent), lowers the "freezing point" considerably.

The "freezing point" and the interval between the "freezing point" (liquidus) and "melting point" (solidus) affect the fluidity (or flowing power) of the steel. If the steel is fluid, the elimination of gases and nonmetallic inclusions is favored. Fluidity is also affected by the presence of some alloying elements. Chromium steels are especially sluggish during pouring, probably because of the presence of oxide films. The fluidity of the metal will be reflected in general surface condition by its effect on the mechanics of pouring, such as splashes, umbrella streams, and the rate of teeming. Splashes may cause scabs, and the formation of ingot cracks is affected by teeming rates.

Fig. 5 illustrates a scabby bloom surface, which generally is associated with splashes caused by poor teeming practice. Fig. 6

equally spaced (in respect to the mold salients) under the skin of the ingot. Flute cracks can generally be traced to hot heats or high teeming rates.

Crystallization Characteristics and Segregation.—The chemical composition has a pronounced effect on the crystallization and segregation of ingots, along with other factors. The primary cause of heterogeneity is differential freezing. Carbon, sulphur and phosphorus, elements producing a wide range between solidus and liquidus, show the greatest segregation. Silicon, manganese, nickel and copper show the least because they produce a narrow range between solidus and liquidus. The forces of differential freezing are modified further by the effect of chemical composition on the thermal and physical properties of the steel, such as heat conductivity, specific heat, density, shrinkage, the latent heat of solidification and latent heat of solid transformations. Also, the diffusion rates of the

various elements are important, that of carbon being high and those of silicon, phosphorus and manganese low.

chromium, nickel, molybdenum, tungsten, have characteristic columnar and dendritic structures. Small additions of some ele-

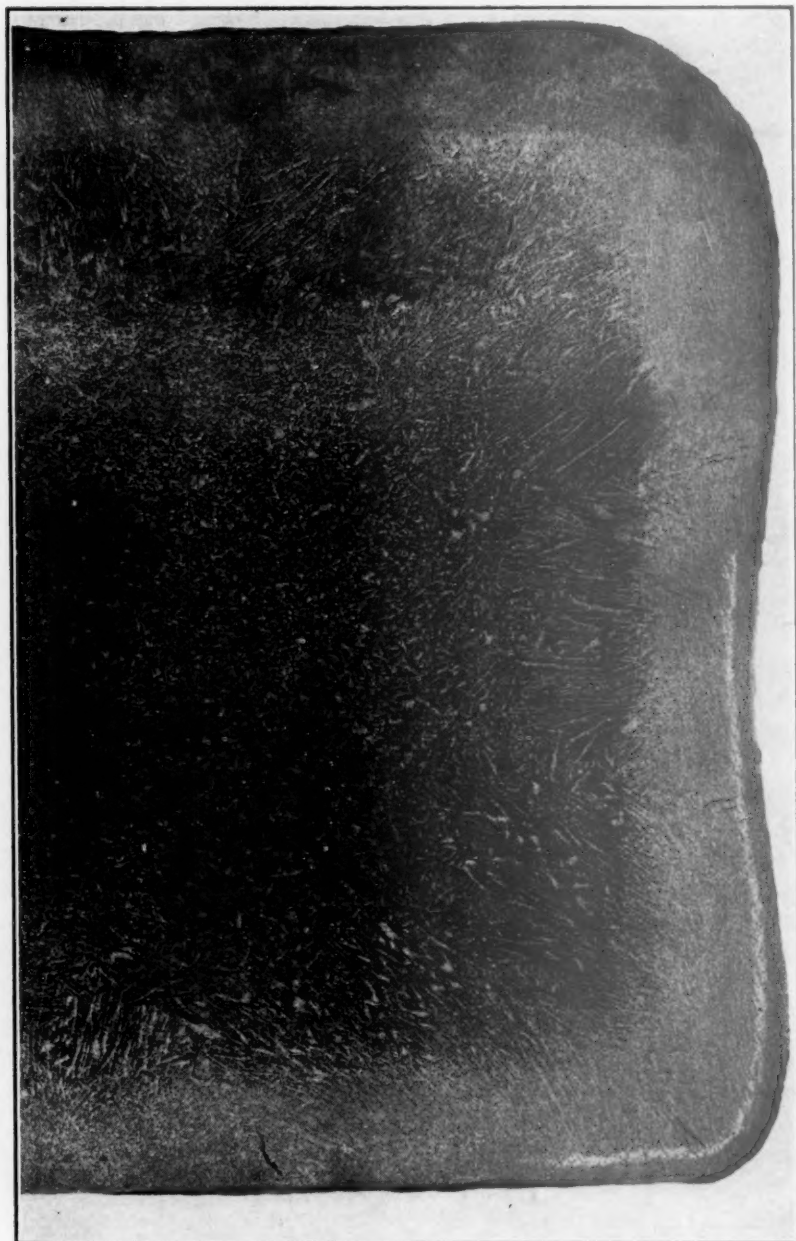


FIG. 6.—TRANSVERSE BLOOM SECTION OF S.A.E. 2315 STEEL, SHOWING FLUTE CRACKS.

The combination of all these factors affects the course of crystallization. Characteristic structures are found in many steels; those high in alloying elements such as

ments such as titanium, columbium and vanadium, which form highly insoluble carbides, may act as nuclei and materially change the cast structure.

The Seventh Report on the Heterogeneity of Steel Ingots¹ is an excellent reference on solidification, crystallization and segregation of steel ingots.

are found where the crystals growing from two faces meet, as in the columnar zone of ingots. The following illustrations indicate that stresses and lines of weakness in the

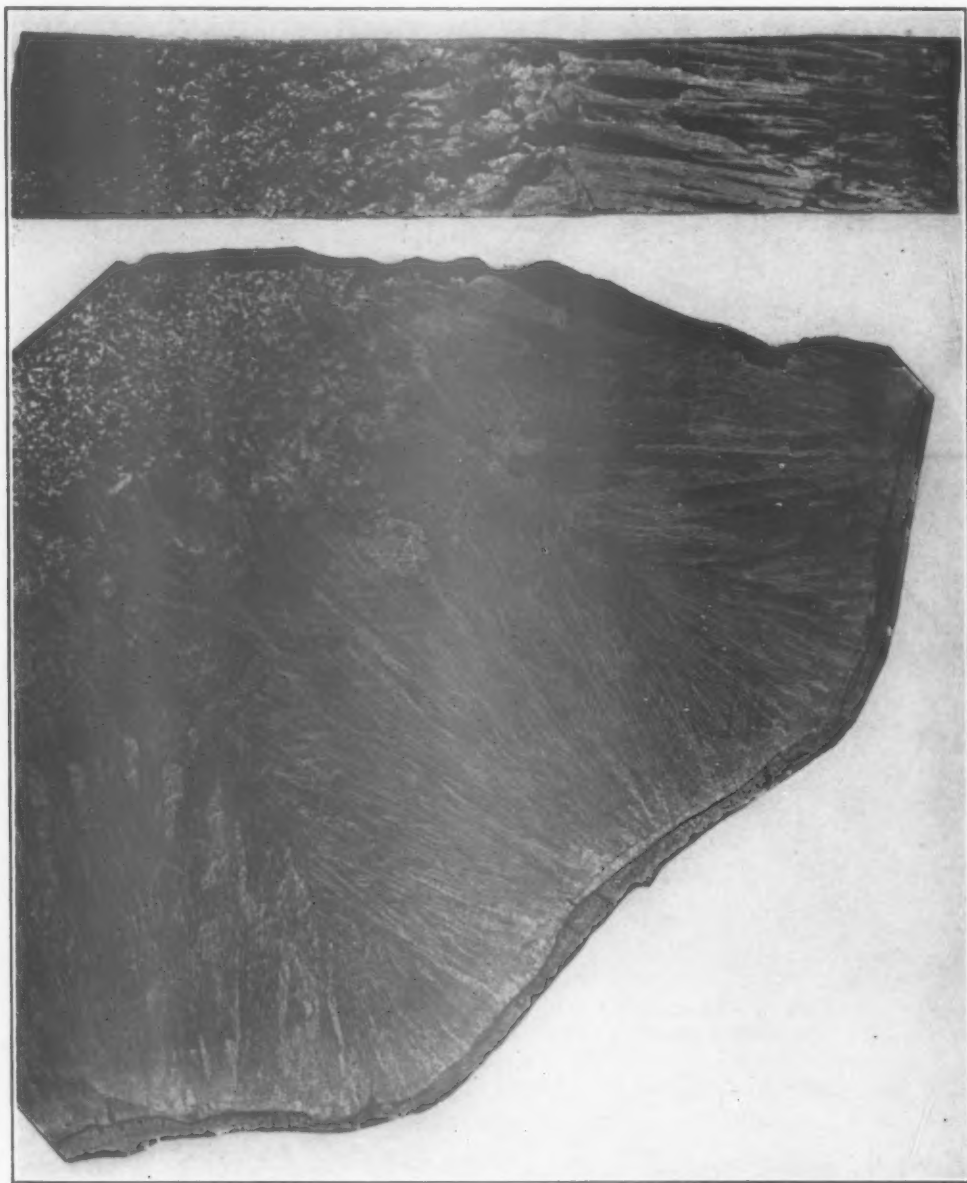


FIG. 7.—TRANSVERSE INGOT SECTION OF S.A.E. 3312 STEEL.

Note parting between skin and columnar zone. In fractured section columnar crystals are directed slightly upward.

The cast structure has a decided influence on the hot-working properties and surface characteristics of steel. Planes of weakness

ingot may later be manifested in surface defects or poor hot-working qualities. Fig. 7 is a transverse ingot section of S.A.E. 3312 steel with a fracture taken across the slice.

¹ References are at the end of the paper.

Note parting between the skin and the pronounced columnar zone. Columnar crystals are directed slightly upward. Fig. 8 shows the same type of steel with a flute

decreases with increasing temperature. The modulus of elasticity and modulus of rigidity of metals decrease with increasing temperature. In general, the plastic work-



FIG. 8.—TRANSVERSE INGOT SECTION OF S.A.E. 3312 STEEL.
Note flute crack at intersection of columnar crystals.

crack at the intersection of the columnar crystals.

EFFECT OF CHEMICAL COMPOSITION ON HOT-WORKING PROPERTIES AND SURFACE CHARACTERISTICS OF STEEL

Plastic Hot-working Range.—Various factors influence the magnitude of the forces under which a material will yield plastically, according to Nadai.² The magnitude of stress necessary to produce plastic flow

ing properties of pure metals of the same structure are similar, at the same ratio of the absolute hot-working temperature to the absolute melting temperature. By dissolving a foreign substance in a metal the resistance to plastic deformation may be greatly changed.

The practical hot-working range of steel lies between the minimum temperature at which the steel can be deformed without rupture or breakage with the available

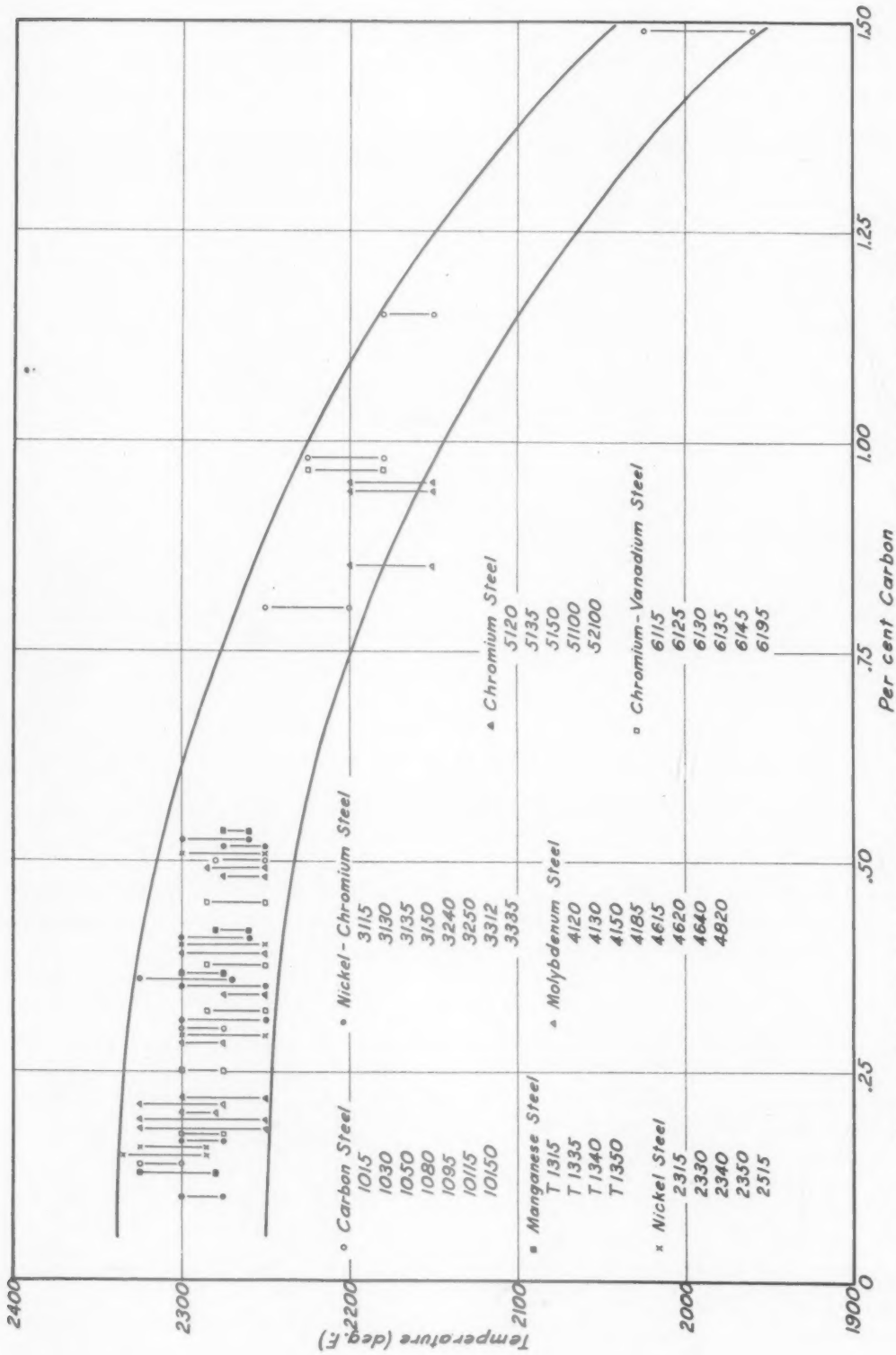


FIG. 9.—SOAKING-PIT DRAWING TEMPERATURE VERSUS CARBON CONTENT OF VARIOUS S.A.E. STEELS.

equipment and the upper temperature limitation where "burning" may occur. This range may be narrow with some steels, with others it is fairly wide. The hot-

ance to deformation of high-carbon steel may be lower than low-carbon steel. For customary rolling temperatures, however, the resistance to deformation increases with

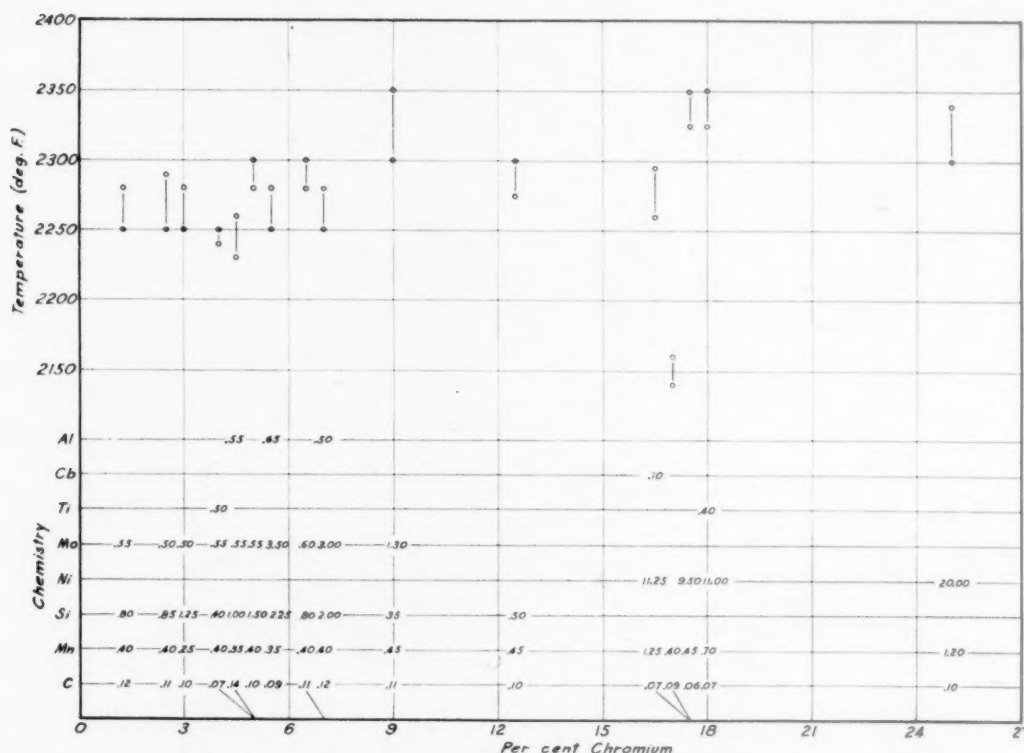


FIG. 10.—SOAKING-PIT DRAWING TEMPERATURES VERSUS CHROMIUM CONTENT FOR VARIOUS CORROSION AND HEAT-RESISTING STEELS.

working range is largely controlled by carbon content and to a lesser extent by the presence of other alloys. Fig. 9 shows the soaking-pit draw temperatures of a variety of alloy steels that have been successfully reduced from ingots to blooms on a blooming mill with minimum surface-conditioning costs. The relation of chromium content to soaking-pit draw temperature for a number of high-temperature and corrosion-resisting steels is shown in Fig. 10. Carbon is the dominant factor in regard to draw temperatures, with the other alloys exerting only a minor influence.

At low temperatures (below 1600°F.) steels of high carbon content have a higher resistance to deformation than low-carbon steels. With high temperatures the resist-

increasing carbon content, inasmuch as the rolling temperature of steels with higher carbon contents is lower.

High-alloy steels, such as the austenitic types, have several times the resistance to deformation of plain carbon steels. In high-alloy steel, with high reductions by rolling, the resistance to deformation may be higher than the resistance to rupture, so that cracking may occur. This is very well illustrated in Fig. 11, representing the ruptured surface of a bloom of 25 per cent Cr-20 per cent Ni steel that was rolled too cold.

Resistance to deformation drops rapidly for all steels as the temperature is increased; however, a low temperature may

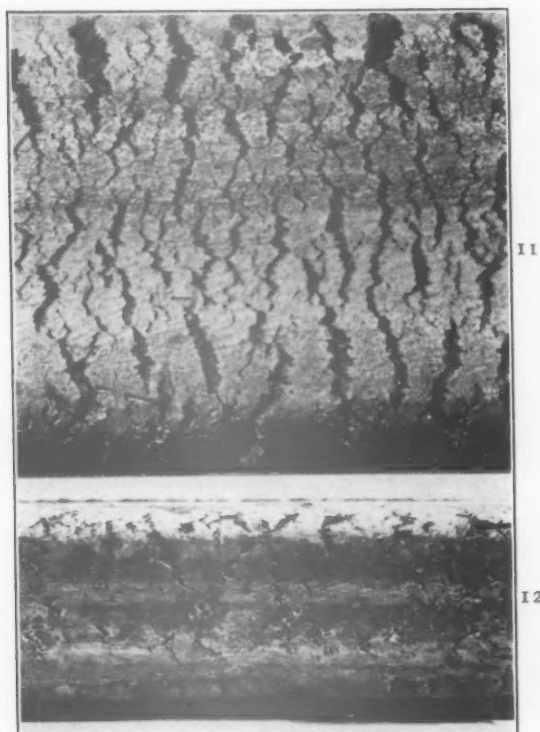


FIG. 11.—RUPTURED SURFACE OF BLOOM THAT WAS ROLLED TOO COLD.
25 per cent Cr, 20 per cent Ni.

FIG. 12.—BLOOM SURFACE OF BURNT INGOT. S.A.E. 4615 STEEL.

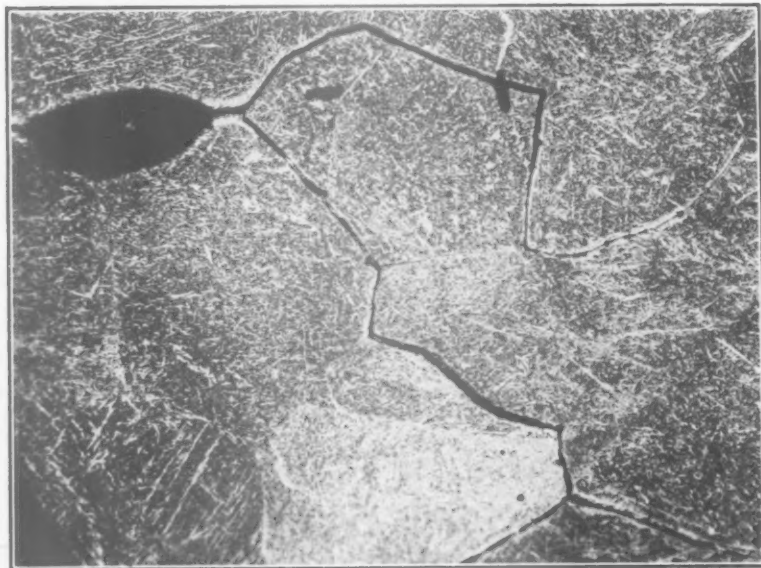


FIG. 13.—BURNT 1.50 PER CENT PLAIN CARBON STEEL. $\times 100$. NITAL ETCH.
Note fused material in grain boundaries.

be desirable for holding section, and lessening scaling and decarburization.

Spreading is affected to a marked degree by composition next to other factors such

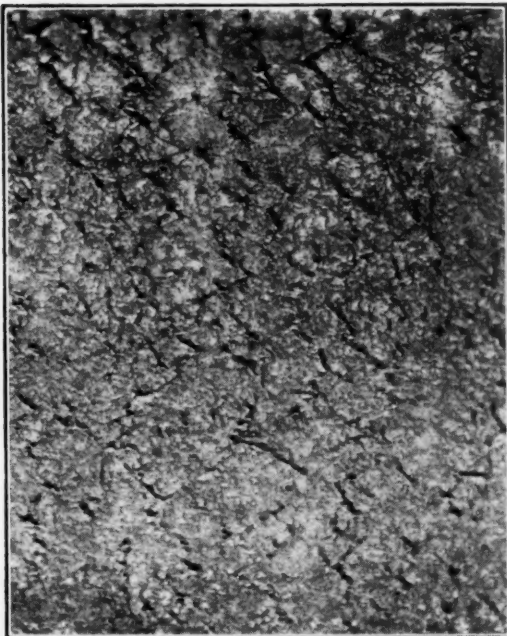


FIG. 14.—BLOOM SURFACE OF S.A.E. 52100 STEEL SHOWING EFFECT OF TIN CONTAMINATION.

as rolling speed, temperature, roll diameter and roll surface. Ferritic chromium steel and high-silicon transformer steel show the greatest spread of the common alloy steels. Forward slip* drops little with increasing rolling temperature with carbon steels, while it shows an appreciable drop with high-alloy steels.

The upper limits of hot-working temperature are determined by the temperature at which fusible constituents in the steel will melt and penetrate into the grain boundaries and leave voids between the grains. The theoretical upper limit for plain carbon steels is the solidus line of the iron-carbon diagram. Alloy content affects the position of the solidus line slightly but carbon exerts the greater effect. Fig. 12

* Forward slip—a forward flow at a higher velocity than the peripheral speed of the rolls, depending in a large measure on the friction of the rolls.

shows the bloom surface from a burnt ingot of S.A.E. 4615 steel. Fig. 13 is a photomicrograph of a plain carbon steel that has been burnt. The fused material shown at the grain boundaries may cause separation of the grains when steel is hot-worked.

Certain elements may produce hot-shortness or cause surface defects in steel. Sulphur, tin, arsenic, antimony and boron will produce hot-shortness; the degree may vary with the carbon content of the steel and the presence of other elements. If such elements are present in undesirable amounts, the hot-working range is narrowed to such a degree that often the steel cannot be hot-worked satisfactorily.

High sulphur content in steel may cause hot-shortness. Proper deoxidation and sufficiently high manganese content will lessen hot-shortness in sulphur steels. The method of addition of sulphur is also known to have an effect.

Little is known of the cause of red-shortness produced by antimony, arsenic and tin, although 2 per cent will close the gamma loop. Tin contents as low as 0.15 per cent will definitely affect the surface condition of steel. Fig. 14 illustrates such a condition. Antimony in the amount of 0.15 per cent has been reported by FonDersmith³ to cause hot-shortness.

Fig. 15 is a photomicrograph of an S.A.E. 52100 steel containing 0.026 per cent boron. This heat broke up completely in the blooming mill, although draw temperatures ranging from 1900° to 2200°F. were used. Note the low-melting constituent that formed in the grain boundaries, and the crystals of the material that formed on cooling.

Copper will produce poor surface on steel unless sufficient nickel or molybdenum is present. Fig. 16 illustrates an interesting example of the effect of copper penetration on hot-shortness. A small amount of material from a bronze guide roll in the reeling operation was rubbed off onto the surface of the tubes that had been pierced.

On reheating for the sinking operation the bronze (60 per cent Cu) penetrated into the surface of the tubes, causing spiral cracks on subsequent hot-working.

though the ferritic structure (delta iron) is found in certain types such as the high-chromium steels. Mixed phases consisting of austenite and ferrite (delta iron) may



FIG. 15.—S.A.E. 52100 STEEL CONTAINING 0.026 PER CENT BORON. $\times 1000$. NITAL ETCH.
This heat broke up in blooming mill, because of hot-shortness.



FIG. 16.—EFFECT OF COPPER PENETRATION ON HOT-SHORTNESS.
Note spiral cracks on surface of tube.

Phase Structures at Hot-working Temperatures.—Most steels have an austenitic structure at hot-working temperatures al-

though the ferritic structure (delta iron) is found in certain types such as the high-chromium steels. Mixed phases consisting of austenite and ferrite (delta iron) may occur at hot-working temperatures. Undissolved carbides and nonmetallic inclusions (oxides, silicates, sulphides, nitrides, etc.)

may also be present. Mixed phases generally result in poor hot-working characteristics.

This range has been studied by F. Wever.⁴ E. J. Davis⁵ has classified the distribution of elements at elevated temperatures in

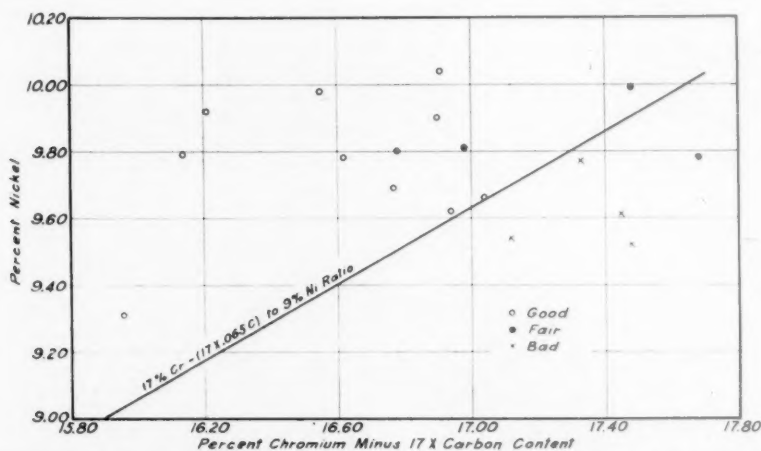


FIG. 17.—PIERCING OF 18-8 + Ti STEEL. EFFECT OF PHASES PRESENT AT PIERCING TEMPERATURE.

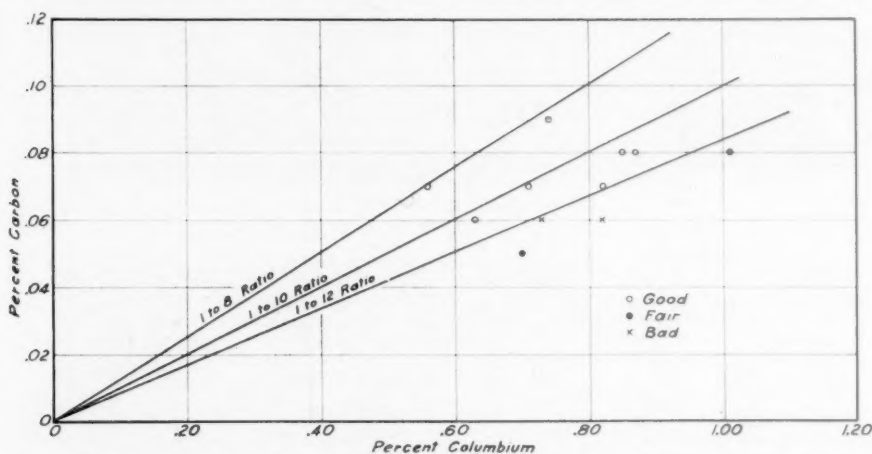


FIG. 18.—PIERCING OF 18-12 + Cb STEEL. EFFECT OF COLUMBIUM-CARBON RATIO.

Fig. 17 shows the effect of mixed phases, austenite and delta iron, on the pierceability of 18 per cent Cr-8 per cent Ni steel with titanium. The austenite-forming phases, nickel and carbon, are plotted against the ferrite-forming phase, chromium. It is to be noted that heats above the 17 per cent Cr-9 per cent Ni (with 0.065 C) ratio pierced well, but that difficulties were experienced with heats below this ratio that contained some delta iron.

The effect of the various alloys on the position of the A_3 and A_4 transformations of iron, thus defining the gamma or austen-

steel as: (1) dissolved in the gamma iron solid solution; (2) combined with carbon to form persistently insoluble carbides; (3) combined with other elements to form special compounds or nonmetallics.

The most insoluble (inactive) state forms preferentially until one or the other element involved approaches depletion, after which the element concentrates in the remaining possible combinations.

The ratio of columbium to carbon in the piercing of 18 per cent Cr-12 per cent Ni steel is an example of this principle, as shown in Fig. 18. When the ratio of

columbium to carbon exceeds 12:1 poor piercing is the result, as illustrated in Fig. 10. Evidently this is due to the for-

and density. Not only must the general effect of physical properties be considered but also the thermal stresses that are set

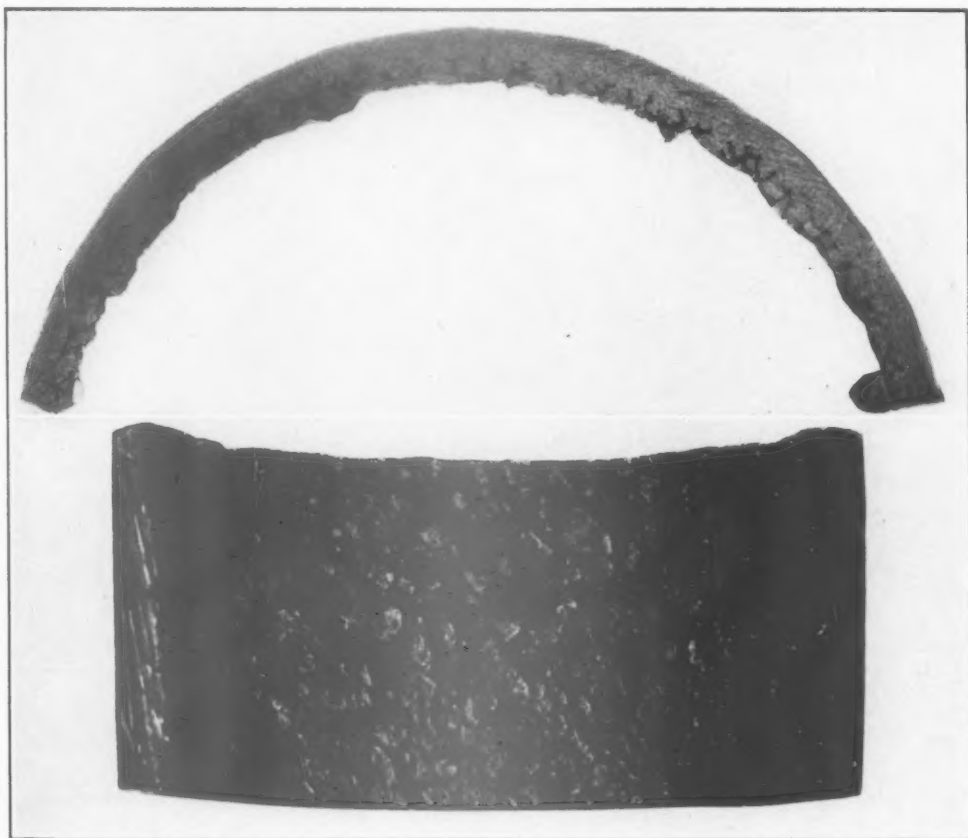


FIG. 10.—SURFACE DEFECTS ON INSIDE OF TUBE; 18-12 STEEL WITH COLUMBIUM.

mation of columbium oxide after the carbon has been satisfied by sufficient columbium.

Rate of Heating.—The rate and amount of heating of ingots is determined by the extent of cooling that has occurred after the ingots are solidified and by the chemical composition as affecting the physical characteristics of the steel. Cold steel may be heated for rolling or forging in ingot form or as blooms, billets or bars. Ordinarily more care must be taken in heating ingots because of their size and the segregated structure resulting from casting.

The physical properties affected by chemical composition as influencing the rate of heating and cooling are thermal expansion, heat conductivity, specific heat,

up by either cooling or heating through the critical range.

The rate of heating or cooling for different alloy steels, other than through the critical range, is not affected greatly by thermal expansion. Values for thermal conductivity of various steels, from data of Shelton and Swanger,⁶ are shown in Fig. 20. At low temperatures the high-alloy steels have much lower thermal-conductivity values than plain carbon steels, but all steels appear to approach a common value at higher temperatures.

The specific heat of iron increases at a fairly rapid rate to the critical range; there is a momentarily large increase to the A_2 transformation, then a rapid drop to the

A₃ transformation, with a slow increase in the gamma range to the A₄ transformation. Specific heat of steel is increased to a fair degree by nickel content and slightly by

cent Ni columbium-steel ingot, which broke up in the blooming mill. It was observed that the center appeared much hotter than the outside. By cooling the

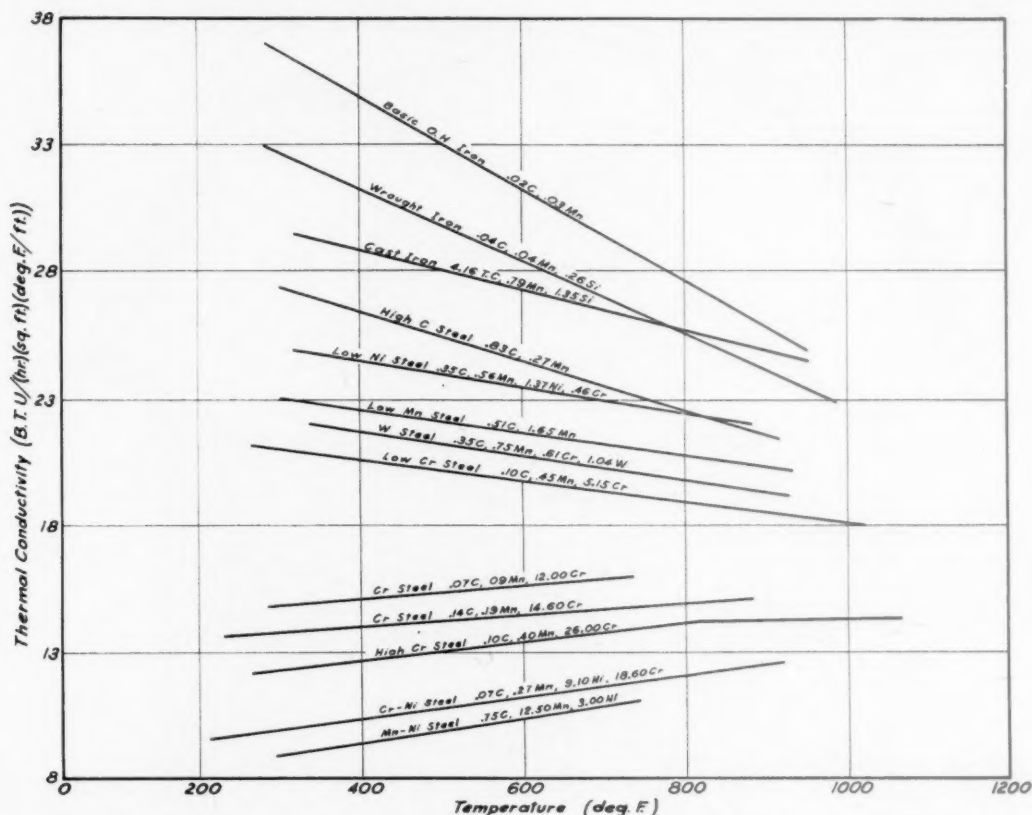


FIG. 20.—THERMAL CONDUCTIVITY OF FERROUS METALS. (After Shelton and Swanger.)

silicon content. The values for the density of steel are of especial importance at the alpha and gamma critical transformation.

Steels high in chromium and nickel content (stainless steels) appear to have low thermal-conductivity values compared to carbon steels. These steels must have lower heat-diffusivity values, for it is necessary that they be heated and "soaked" for a longer time than plain carbon and low-alloy steels, so that a large differential of temperature does not exist between the center and surface of the section being heated. Conversely, it is to be noted that the center lags considerably behind the outside on cooling. Fig. 21 shows the transverse section of an 18 per cent Cr-12 per

ingots for a greater time before charging them into the soaking pits, and by use of lower heating temperatures this type of steel was bloomed successfully. Note the weak appearance of the extensive columnar zone.

Thermal stresses set up by transformations through the critical range are important—not only the amount of volume change, but also the temperature differential between various parts of the section, especially in the cast structure of ingots and the temperature at which the transformation takes place. The transformation temperatures are generally lowered by carbon, manganese, and nickel. A slow rate of cooling or heating through the critical



FIG. 21.—TRANSVERSE FRACTURED SECTION OF INGOT THAT BROKE IN BLOOMING MILL; 18-12 STEEL WITH COLUMBIUM.

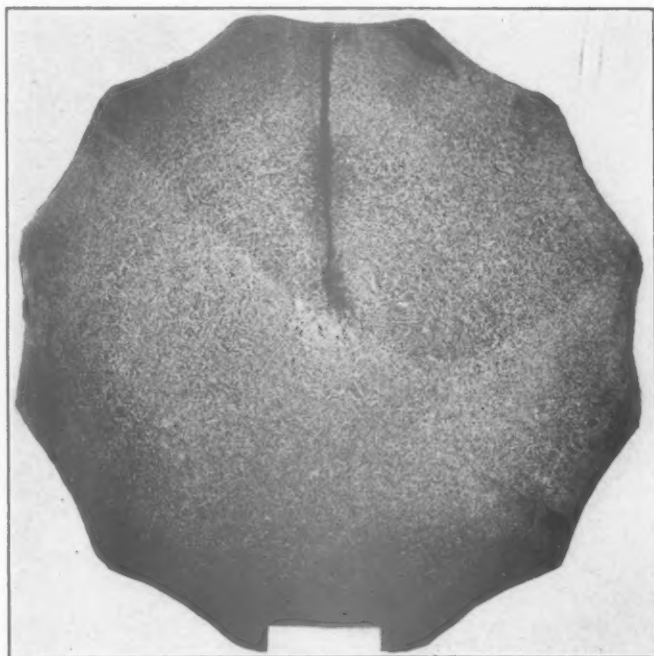


FIG. 22.—TRANSVERSE SECTION OF INGOT OF S.A.E. 3245 SHOWING LONGITUDINAL CRACK.

range is necessary if longitudinal cracks are to be avoided in certain steels. Figs. 22 and 23, ingot sections of S.A.E. 3245 steel, illustrate the type of crack caused by

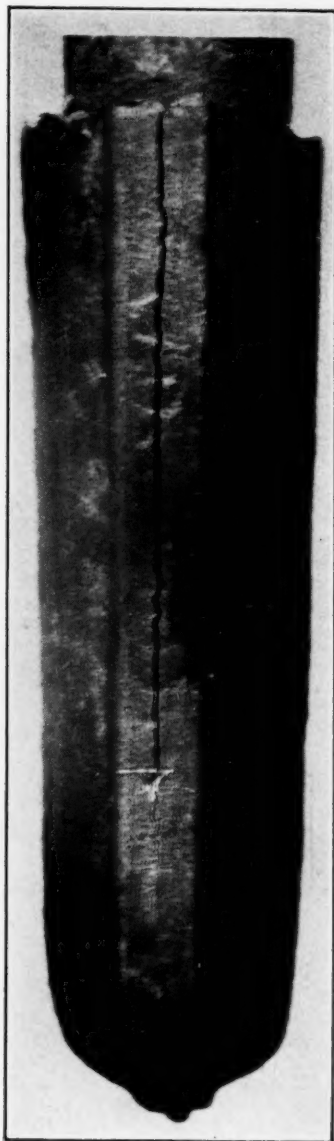


FIG. 23.—INGOT OF S.A.E. 3245 STEEL SHOWING LONGITUDINAL CRACK.

cooling stresses which may occur in nickel-chromium steels of 0.30 to 0.50 carbon. Undoubtedly, a combination of factors, including the cast structure, are responsible for the stresses set up in these steels.

The chemical composition definitely de-

fines the phase structure found at plastic hot-working temperatures as well as the critical range of the steel. Grain growth must be especially considered in the austenitic and ferritic steels. The absence of a transformation at heating temperatures precludes grain refinement due to a phase change produced normally in the pearlitic and martensitic steels by heating through the critical range. Grain coarsening in the austenitic and ferritic stainless steels will occur at temperatures below the hot-working range. Because of their low thermal conductivity these steels must be "soaked out" below the grain-coarsening temperature (1500° to 1700°F.), then raised rapidly in temperature to the plastic working range, as grain coarsening is an important factor and must be avoided.

Cooling Characteristics.—The effect of chemical analysis on thermal and physical properties as well as the position of the critical range control the formation of differential stresses that may occur during cooling. Jagged cracks may develop on the surface of rolled sections during cooling (Fig. 24).

The tendency to harden on air-cooling may directly affect clean-up costs; owing to an increased surface hardness. Steels of over 0.35 to 0.40 carbon will be harder under the chipping hammer when air-cooled in bloom form than steels that are slow-cooled.

Phase transformations may be helpful in loosening and cracking off adhering scale by the expansion that occurs when steel is cooled through the critical range. Phase transformations as influenced by the manner of cooling may be manifested in surface difficulties in subsequent hot-forming operations. High-carbon graphitic steels must be cooled quickly in air; otherwise graphite is precipitated and difficulties may be experienced in hot-working the steel. Certain austenitic steels must be cooled quickly in order to retain the proper phase structure.

Scale Formation.—The scaling characteristics of various steels are largely determined by chemical composition. Published researches have been directed mostly to

Surface Decarburization.—Surface decarburization is an important factor in many steels and must be kept to a minimum, especially in medium and high-carbon



FIG. 24.—COOLING CRACK IN BLOOM OF S.A.E. 3140 STEEL.



FIG. 25.—SCABS CAUSED BY "ROLLED IN SCALE." BLOOM OF S.A.E. 2315 STEEL.

studies of scaling losses for long periods of time at temperatures below those used in the hot-working of steel. The amount of scale formed in the comparatively short times required for heating ingots and billets for rolling and forging does not vary considerably between various alloy steels. However, the adherence of the scale to the steel and its ability to flake off in the rolling or forging operation is very important. Tightly adherent scale is characteristic of nickel steels. Fig. 25 illustrates a scabby condition in a bloom of S.A.E. 2315 steel caused by "rolled in" scale.

steels where the stock cleanup on the finished product is not sufficient to remove the decarburized zone. It is altogether possible that a highly decarburized steel may not hot-work properly because of the difference in composition of surface and interior.

Surface decarburization is lessened by chromium, titanium, and vanadium, and it is increased by nickel and molybdenum, at temperatures of hot-working. It must be kept in mind that decarburization is affected by time, temperature, and heating atmosphere to a large degree, consequently the heating times and temperatures re-

quired for certain alloy steels may be such that the rate and degree of decarburization is increased.

SUMMARY

The chemical composition of killed steel has a decided effect on its hot-working properties and surface characteristics. Composition limits the state of deoxidation, influences the gas content, and controls the freezing range. It also determines the physical properties of the steel that modify the thermal behavior of the ingot during solidification. The combination of these factors control to a large extent the crystallization characteristics and cast structure of the metal.

The phase structure and hot-working properties of steel are influenced and

limited by chemical composition. Physical properties restrict the rate of heating and cooling of the steel; especially in the transformation range. The extent of scaling and surface decarburization is modified by the chemical composition of the steel. Examples showing various surface defects in alloy steels have been discussed.

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Effect of Composition and Steelmaking Practice on Graphitization below the A_1 of Eighteen One Per Cent Plain Carbon Steels

By CHARLES R. AUSTIN AND MAURICE C. FETZER*

(New York Meeting, February 1940)

It has long been known that plain high-carbon steels may be susceptible to graphitization below the A_1 critical, but no data have been available to indicate what factors cause and tend to inhibit graphite formation. Two recent publications^{1,2} have shown that the factors controlling graphitization below the A_1 are different from those operating above the A_1 inversion where commercial graphitization of malleable iron begins. Furthermore, for plain high-carbon steels graphitization below the critical point does not appear to be related to ordinary chemical analyses.

Many years ago it was recorded³ that the rate of graphitization at subeutectoid temperature is not a maximum just below the A_1 critical, but at some lower temperature, which Austin and Norris have shown to be about 670°C. Indeed, work done in our laboratory has demonstrated that it is impossible to spheroidize certain steels in the temperature range of 650° to 710°C. without the formation of considerable amounts of graphite. However, if the temperature is maintained just below the A_1 (720°C.) these same steels may be completely spheroidized at constant temperature.

In previous studies^{1,2,4} on 1 per cent plain carbon steels graphitization was encountered during prolonged tempering. The limited number of steels studied did not provide sufficient data to permit adequate

study of the factors controlling this graphitization. Accordingly, a limited statistical investigation was undertaken, utilizing 18 steels of similar chemical analyses, furnished by four steel companies, who also supplied information regarding the history of manufacture.

An extensive program of research is being carried out on these steels, including the effect of pretreatment and atmosphere on the nature and extent of graphitization, and the possible correlation of graphitization with such characteristic properties as hardenability, grain size and mechanical behavior.

In the present paper discussion is restricted to a study of the correlation between graphitizing tendency at 670°C. after quenching from several temperatures above the critical, and (1) the minor variations in the chemistry of these steels of "similar" chemical composition, and (2) the deoxidation practice employed. The state of the lead bath, oxidized or protected from oxidation by charcoal, used in the tempering treatments is also considered.

MATERIALS

Eighteen plain carbon steels of about 1 per cent carbon, and containing similar amounts of each of the other common elements usually found as impurities, were obtained in the form of rods $\frac{3}{8}$ in. in diameter from four steel manufacturers. The analyses for ordinary and special elements of all the steels were made on the rod stock as received in the laboratory, and the re-

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¹ References are at the end of the paper.

sults are recorded in Table 1. Twelve of these were arc electric; three induction electric; and three basic open-hearth steels. The aluminum additions in pounds per ton and the time of adding this aluminum are given in Table 6. The manufacturers endeavored to maintain the carbon, silicon, sulphur, phosphorus and manganese analyses within the certain narrow limits requested, and in most instances furnished samples from three similarly prepared heats. These three samples represented extremes and a mean behavior in any test, such as hardenability, selected by the company. They may be regarded as triple samples of a steelmaking process.

HEAT-TREATMENTS

The eighteen steels were water-quenched from each of five different heat-treatments prior to annealing at 670°C. These conditions are given in Table 2.

Immediately after quenching, the pieces were tempered at 200°C. for 1 hr. This treatment lowered the hardness from about Rockwell C66 to C61. Samples of specimens from each quench were then heated for 125

and 600 hr. at 670°C. in a lead bath covered with charcoal. Another set (from quenches 1, 2, 3 and 4) was heated for 125 hr. at 670°C. in lead that had no surface protection from atmospheric oxidation. All tempered specimens were finally air-cooled.

After the 600-hr. treatment in covered lead, the specimens were free from scale and surface decarburization, whereas after only 125 hr. in lead subject to atmospheric oxidation the samples were heavily scaled but still free from evident decarburization.

All specimens were then cut transversely and tested for Rockwell B hardness, the results being given in Table 3 for the samples tempered for 600 hr. in covered lead, and in Table 4 for those tested in the unprotected lead bath for only 125 hr. The figures recorded represent the average of several observations. Longitudinal and transverse pieces also were cut for metallographic examination.

GRAPHITIZATION STUDIES ON TEMPERING IN COVERED LEAD

Considering first the results of hardness determinations obtained when the lead was

TABLE 1.—*Manufacture and Chemical Analysis*^a
PER CENT

Steel	C	Si	Mn	S	P	Cr	Ni	Cu	Oxygen over that in Al ₂ O ₃ (calc.)	N	Al (metallic)	Al ₂ O ₃	Oxygen (total)	Kind
H	1.08	0.33	0.36	0.017	0.020	0.11	0.04	0.12	0.0022	0.0065	0.010	0.006	0.005	Basic arc electric
I	1.02	0.27	0.22	0.010	0.014	0.09	0.04	0.13	0.0051	0.0070	0.005	0.004	0.007	Basic arc electric
J	1.03	0.27	0.31	0.020	0.017	0.10	0.04	0.10	0.0011	0.0045	None	0.002	0.005	Basic arc electric
K	1.00	0.45	0.30	0.022	0.020	0.06	0.06	0.13	0.0125	0.0070	None	0.001	0.013	H. F. induction ^b
L	1.07	0.31	0.26	0.010	0.020	0.09	0.06	0.15	0.0061	0.0059	0.003	0.004	0.008	H. F. induction ^b
M	1.00	0.20	0.18	0.021	0.017	0.08	0.04	0.17	0.0017	0.0093	0.010	0.007	0.005	Basic arc electric
N	1.12	0.20	0.25	0.013	0.017	0.04	0.13	0.13	0.0002	0.0101	0.007	0.008	0.004	Basic arc electric
O	1.06	0.13	0.19	0.010	0.016	0.03	0.06	0.13	0.0017	0.0097	0.010	0.008	0.0055	Basic arc electric
P	1.07	0.14	0.22	0.010	0.017	0.07	0.07	0.15	0.0018	0.0101	0.003	0.006	0.0045	Basic arc electric
R	1.01	0.28	0.34	0.021	0.010	0.06	0.10	0.08	0.0021	0.0034	0.001	0.004	0.004	Induction ^c
S	1.03	0.21	0.24	0.017	0.017	0.04	0.04	0.15	0.0023	0.0104	0.004	0.006	0.005	Basic arc electric
T	1.01	0.21	0.21	0.019	0.012	0.10	0.08	0.13	0.0002	0.0042	0.003	0.007	0.0035	Basic open hearth
U	1.02	0.20	0.27	0.016	0.013	0.11	0.10	0.16	None	0.0042	0.020	0.009	0.0035	Basic open hearth
V	1.03	0.20	0.20	0.023	0.013	0.11	0.06	0.13	None	0.0034	0.002	0.008	0.0035	Basic arc electric
W	1.03	0.21	0.18	0.020	0.010	0.09	0.03	0.19	None	0.0039	0.018	0.010	0.0045	Basic open hearth
X	0.99	0.24	0.22	0.017	0.015	0.04	0.02	0.11	0.0003	0.0084	0.019	0.011	0.0055	Electric
Y	1.03	0.22	0.20	0.014	0.012	0.05	0.02	0.06	0.0002	0.0031	0.004	0.009	0.0045	Electric
Z	0.98	0.19	0.20	0.017	0.014	0.04	0.04	0.04	0.0023	0.0014	0.004	0.010	0.007	Electric

^a Molybdenum and cobalt were reported as 0.0 per cent and vanadium as less than 0.01 per cent on all 18 steels. Traces of titanium were reported on steels R, V and Z but it was nil in the other 15 steels.

^b Magnesia crucible.

^c Acid crucible, no slag.

covered (Table 3), the data indicate two obvious groupings of the steels regardless of the pretreating quench conditions. Thus the steels in group 1, represented by steels H to R, softened to a more or less similar hard-

TABLE 2.—*Pretreating Conditions Prior to Quenching*

Quench Designation	Heated to, Deg. C.	Time Held	Conditions of Heat-treatment
1	1000	1 hr.	Packed in charcoal
2	850	10 min.	Heated in electric muffle
3	850	24 hr.	Packed in charcoal
4 ^a	800	24 hr.	Packed in charcoal
5 ^b	750	10 min.	Heated in electric muffle

^a Steels H, J, L, N and P were not included.

^b Because of the low temperature and short time the specimens for treatment, No. 5 were first normalized.

ness value of about Rockwell B86, whereas group 2, represented by steels S to Z, exhibited varying degrees of greater temperature softening, although the relative hardness was dependent on pretreatment. Furthermore, it may be noted that this (general) greater softening of the steels in group 2 on prolonged tempering at 670°C. was obtained irrespective of both time and temperature of anneal prior to quenching.

Metallographic examination showed that all steels in group 2 graphitized to varying

degrees but the steels in group 1 showed no evidence of graphitization. Fig. 1, illustrating the microstructure of steel H at 1000 dia. after 600 hr., is typical of group 1. Although this sample was annealed for 1 hr. at 1000°C. and then water-quenched, the photomicrograph is typical of the tempered structure of all the prequenched samples for steels in group 1 as listed in Table 3. Since steels in group 2 graphitized to varying extents, it is not possible to select a typical example. However, in Fig. 2, which illustrates the structure of steel Z after a water quench from 1 hr. at 1000°C. followed by the 600-hr. treatment at 670°C. an example of almost complete graphitization is presented. The specimen was etched to bring out any spheroidized cementite but not deeply enough to reveal the ferritic grain size. An unetched section of the sample at 200 diameters shows more clearly the amount and distribution of the graphite (Fig. 3).

Chemical Analysis

In order to permit a study of the possible correlation between the chemistry of the steels and their graphitizing tendency on prolonged heating at 670°C., the steels

TABLE 3.—*Rockwell B Hardness of the 18 Steels after 600 Hours at 670°C. in Charcoal-covered Lead*

Prior Heat-treatment	Quenched from 1000°C. 1 Hr.	Quenched from 850°C. 10 Min.	Quenched from 850°C. 24 Hr.	Quenched from 800°C. 24 Hr.	Quenched from 750°C. 10 Min.
Group 1					
H.....	88	87	86		89
I.....	86	85	83	82	85
J.....	87	85	86		87
K.....	87	86	85	84	87
L.....	87	85	84		87
M.....	86	87	87	85	87
N.....	86	84	84		87
O.....	86	85	84	80	85
P.....	86	84	85		86
R.....	86	86	86	83	86
Group 2					
S.....	50	52-57 ^a	49-63	54-61	63
T.....	48	54	55	55-63	68-73
U.....	61	63-67	63	66-78	79
V.....	46	48-59	49-59	56-65	71
W.....	43	45	47	52	60
X.....	42	45	47	47	65
Y.....	46	49	45	50	55
Z.....	38	39-43	39	40-46	36-43

^a The smaller of the two values was nearly always obtained at the center of the specimens.



FIG. 1.—TRANSVERSE SECTION, STEEL H.
× 1000. ETCHED.

Structure: spheroidized cementite with no graphite. Treatment: 600 hr. at 670°C. in lead

have been arranged in Table 5 in order of increasing percentage of carbon, manganese, silicon, sulphur, phosphorus, chromium, nickel, copper, metallic aluminum, alumina, nitrogen, total oxygen, and oxygen in excess of that required for the formation of the alumina. The steels that graphitize are shown in bold face italic.

The tabulated data indicate no complete correlation between the amount of any one element contained in the steels and the tendency for them to behave as graphitizing or stable steels. However, certain general trends may be noted.

Usually it is considered that the higher carbon steels are more prone to graphitize, yet it may be noted from Table 5 that the lower carbon alloys (0.98 to 1.03) are the only ones to exhibit temper graphitization. Thus it may be assumed, in any correlation observed for other elements, that the carbon content is not a disturbing factor.

Considering the distribution of the steels with respect to the amounts of sulphur, chromium, nickel, copper, metallic aluminum and total oxygen, it would appear to be clear that none of these elements functions as a controlling factor in carbide stability or graphitization. However, the amounts of manganese, silicon, phosphorus, nitrogen and alumina seem to show some sort of correlation with carbide behavior. Thus the graphitizing steels group themselves on the low manganese, silicon, phosphorus and nitrogen side and on the high-alumina side. This may be significant as an indication of the effect of steelmaking practice, especially deoxidation, on graphitization.

covered with charcoal, and water-quenched. Pretreatment: 1 hr. at 1000°C. in charcoal and water-quenched. Hardness: 88B.

FIG. 2.—LONGITUDINAL SECTION, STEEL Z.
× 1000. ETCHED.

Structure: retained graphite with practically no cementite. Treatment and pretreatment same as in Fig. 1. Hardness: 38B.

FIG. 3.—LONGITUDINAL SECTION, STEEL Z.
× 200. UNETCHED.

Structure: retained banded graphite. Treatment and pretreatment same as in Fig. 1. Hardness: 38B

The authors take the view that carbon steels of the compositions considered in this investigation may be regarded as normally free from marked tendency toward graphi-

which is low in the stable steels, 0.001 to 0.008 per cent, and high in the graphitizing steels, 0.006 to 0.011 per cent. Furthermore, it has been found in the study on

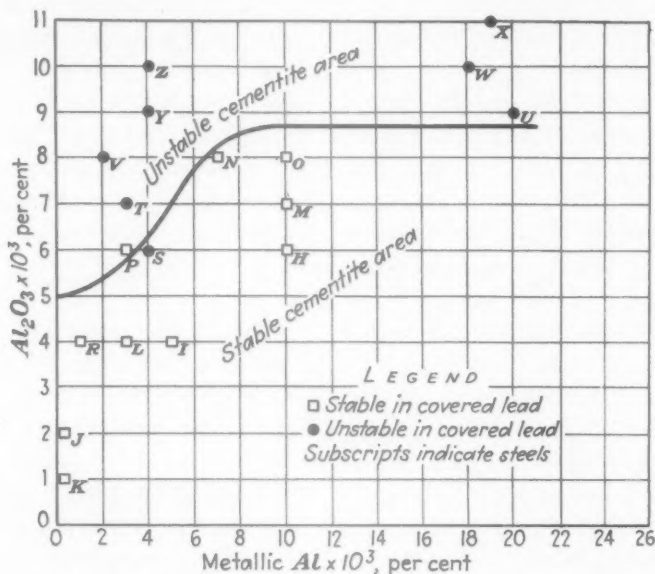


FIG. 4.—ALUMINA-ALUMINUM PLOT FOR THE 18 STEELS.

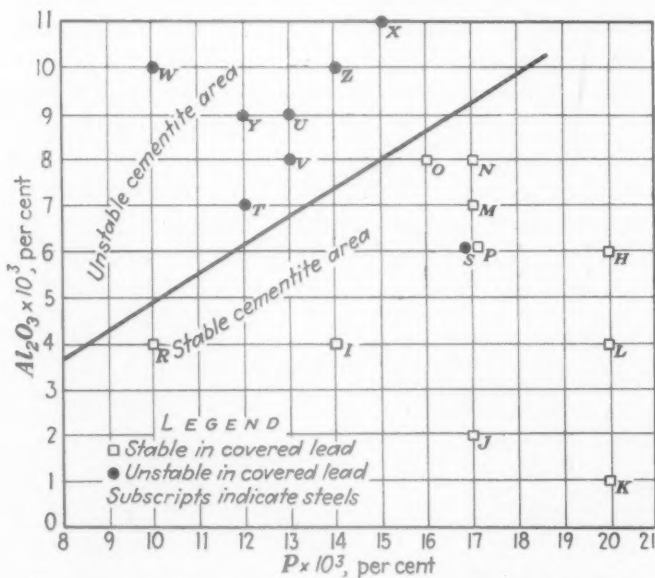


FIG. 5.—ALUMINA-PHOSPHORUS PLOT FOR THE 18 STEELS.

tization and so the most useful purpose of a limited statistical analysis is to ascertain what elements or compounds appear to promote graphitization. The only substance that appears to function in this way is Al_2O_3 ,

these unstable steels that the higher the percentage of Al_2O_3 , the more rapid is the graphitization.

It was thought that an analysis of the tendency toward graphitization, correlated

with two elements considered simultaneously might offer useful results. The analysis was conducted by plotting the 18 steels on rectangular coordinates, with one element as abscissa and the other as ordinate for the various pairs of each of the 13 elements excepting carbon and total oxygen. This analysis included manganese, silicon, sulphur, phosphorus, chromium, nickel, copper, aluminum, alumina, nitrogen, and oxygen in excess of Al_2O_3 . It was possible to make 55 combinations of pairs of analyses in this manner. Of these 55 combinations, only two showed a favorable segregation of stable and graphitizing steels. These two were Al_2O_3 -Al and Al_2O_3 -P, and the distribution of data with reference to analysis is shown plotted in Figs. 4 and 5, respectively. The Al_2O_3 -Al plot shows steels P and S to be slightly out of place but otherwise, as the metallic aluminum increases the quantity of alumina required for graphitization also increases. This observation apparently suggests a carbide stabilizing effect of metallic aluminum. The Al_2O_3 -P plot shows that with the exception of steel S the graphitizers can be separated from the stable steels by a straight line. The indications are that as the phosphorus increases, the quantity of alumina required for graphitization also increases. Again we have an apparent indication of carbide stabilization, by the element phosphorus. Perhaps the

observations regarding the combined effects of Al_2O_3 and Al and Al_2O_3 and P have little significance because a good segregation is shown by Al_2O_3 alone. However, this may be because steels low in phosphorus are found in the graphitizing group while those high in this element are stable (Table 5). It is also of interest to note that most of the stable steels are high in silicon. This correlation between high silicon content and carbide stability on tempering below the critical has previously been reported.¹

Deoxidation Practice

Since it was possible to obtain a limited number of data from the various companies on the deoxidation practice, a careful study was made to ascertain whether such practice could be correlated with the steel behavior during tempering.

In Table 6, selected data show the aluminum additions made in the furnace ladle or mold, as well as the special calcium-silicon alloy added in the furnace to two of the steels. The data are complete for the stable steels (H to R), only partly complete for the graphitizing steels (S to W), and deoxidation practice could not be obtained for the graphitizing electric steels X, Y and Z.

No correlation appears evident between carbide stability and aluminum additions made either in the furnace or in the ladle. However, not one of the stable steels (H to

TABLE 4.—Rockwell B Hardness of the 18 Steels after 125 Hours at 670°C. in Uncovered Lead

Prior Heat-treatment	Quenched from 1000°C. 1 Hr.	Quenched from 850°C. 10 Min.	Quenched from 850°C. 24 Hr.	Quenched from 800°C. 24 Hr.
H	73-79 ^a	88	89	
I	91	86	88	84
J	91	87	87	
K	84	84-88	81-86	87
L	85-89	84-89	78-90	
M	69	72	89	75-85
N	73-78	82-88	89	
O	81-89	79-87	82-87	86
P	89	80-87	88	
R	90	87	86	83-87
S	46-54	65	49-60	60-65
T	61	65	61-65	66
U	64	70	69-73	71
V	60	60-65	63	60-66
W	43	48	38-45	49-56
X	38-44	44	46-71	49-54
Y	38	48	45	53-62
Z	32-36	36-43	26-35	39

^a The smaller of the two values was nearly always obtained at the center of the specimens.

TABLE 5.—*Steels Arranged in Order of Increasing Chemical Analysis Percentage*
STEELS IN BOLD FACE ITALIC GRAPHITIZE IN COVERED LEAD

C, Per Cent	Steel	Mn, Per Cent	Steel	Si, Per Cent	Steel	S, Per Cent	Steel
0.98	Z	0.18	M, W	0.12		0.010	I, L, O, P
0.99	X	0.19	O	0.14	P, O	0.011	
1.00	M, K	0.20	V, Y, Z	0.16		0.012	
1.01	R, T	0.21	T	0.18	Z	0.013	N
1.02	I, U	0.22	I, P, X	0.20	M, N, U, V	0.014	Y
1.03	J, S, V, W, Y	0.23		0.22	S, T, W, Y	0.015	
1.04		0.24	S	0.24	X	0.016	U
1.05		0.25	N	0.26	I, J	0.017	H, S, X, Z
1.06	O	0.26	L	0.28	R	0.018	
1.07	L, P	0.27	U	0.30	L	0.019	T
1.08	H	0.28		0.32	H	0.020	J, W
1.09		0.29		0.34		0.021	M, R
1.10		0.30	K	0.36		0.022	K
1.11		0.31	J	0.38		0.023	V
1.12	N	0.32		0.40			
		0.33		0.42			
		0.34	R	0.44	K		
		0.35					
		0.36	H				

P, Per Cent	Steel	Cr, Per Cent	Steel	Ni, Per Cent	Steel	Cu, Per Cent	Steel
0.010	R, W	0.03	O	0.02	X, Y	0.04	Z
0.011		0.04	N, S, X, Z	0.03	W	0.05	
0.012	T, Y	0.05	Y	0.04	H, I, J, M, S, Z	0.06	Y
0.013	U, V	0.06	K, R	0.05		0.07	
0.014	I, Z	0.07	P	0.06	K, L, O, V	0.08	R
0.015	X	0.08	M	0.07	P	0.09	
0.016	O	0.09	W, L, I	0.08	T	0.10	J
0.017	J, M, N, P, S	0.10	J, T	0.09		0.11	X
0.018		0.11	U, V, H	0.10	R, U	0.12	H
0.019				0.11		0.13	I, K, N, O, T, V
0.020	H, K, L			0.12		0.14	
				0.13	N	0.15	L, P, S
						0.16	U
						0.17	M
						0.18	
						0.19	W

Al (Metallic), Per Cent	Steel	Al ₂ O ₃ , Per Cent	Steel	Oxygen (Total), Per Cent	Steel	Oxygen in Excess of Al ₂ O ₃ (Calculated), Per Cent	Steel	Nitrogen, Per Cent	Steel
None	J, K	0.001	K	0.003	T, U, V	None	N, T, U, V, W, Y	0.0015	Z
0.001	R	0.002	J	0.004	N, P, R, W, Y	0.0005	X	0.0020	
0.002	V	0.003		0.005	H, J, M, O, S, X	0.0010	I	0.0025	
0.003	L, P, T	0.004	I, L, R	0.006		0.0015	M, O	0.0030	Y
0.004	Y, Z, S	0.005		0.007	I, Z	0.0020	H, P, R	0.0035	V, R
0.005	I	0.006	H, S, P	0.008	L	0.0025	S, Z	0.0040	W
0.006		0.007	M, T	0.009		0.0030		0.0045	T, U, J
0.007	N	0.008	V, O, N	0.010		0.0040		0.0050	
0.008		0.009	Y, U	0.011		0.0050		0.0055	
0.009		0.010	W, Z	0.012		0.0060	I	0.0060	L
0.010	H, M, O	0.011	X	0.013	K	0.0070	L	0.0065	H
0.011						0.0080		0.0070	I, K
0.012						0.0090		0.0075	
0.013						0.0100		0.0080	
0.014						0.0110		0.0085	X
0.015						0.0120	K	0.0090	
0.016								0.0095	M, O
0.017								0.0100	N, P
0.018	W							0.0105	S
0.019	X								
0.020	U								

R) received aluminum additions in the mold, whereas the two steels (S and V) to which it could be definitely ascertained that such mold additions were made are graphitizable alloys.

Further, it may be noted, disregarding the three steels made with unknown melting practice (X, Y and Z), the total aluminum added amounted to 0 to 0.88 lb. per ton for the stable steels, and 0.93 to 1.65 lb. per ton for the steels susceptible to graphitization. As regards steel X, Y and Z, it is of interest to note, from the chemical analysis data in Table 1, that X showed the highest aluminum content while the alumina in Y and Z is as high as that of any of the steels investigated.

GRAPHITIZATION STUDIES ON TEMPERING IN UNCOVERED LEAD

Attention has already been directed to the hardness values obtained after tempering for 125 hr. at 670°C. in lead to which atmospheric oxygen had access (Table 4). In contrast to the clearly defined self-grouping with respect to the hardness of the steels annealed in oxygen-free lead (Table 3), it is now difficult to separate, at a glance, the steels that are stable from those that markedly graphitize as indicated by a pronounced fall in hardness. Furthermore, there is a hardness spread in many more of the steels.

Metallographic examination revealed that all of the 18 steels graphitized in uncovered lead, although the tendency was extremely slight for steels I, J and R. Of the steels that were stable in covered lead (H to R), it is observed that those highest in metallic aluminum showed greatest tendency toward graphitization in uncovered lead. Thus the steels that softened most are M, H, N, O, L, P and K, in order listed, and of these M, H, N and O are high in metallic aluminum (Table 7). J and R, which still show resistance to dissociation of iron carbide in the uncovered lead, are very low in metallic aluminum. Steels K and L are interesting in that they exhibit definite graphitization in uncovered lead and yet are low in metallic aluminum. These two steels, however, are the only ones that had additions of the calcium-silicon alloy.

The steels that graphitized in covered lead appear to be still more prone to graphite formation in the oxygen-bearing bath. Thus, in Table 7, the mean of the hardness values of each steel from the varied quenching treatments after 125 hr. in uncovered lead are compared with similar mean hardness values resulting from the same length of time in covered lead. The steels in this table have been arranged in order of decreasing metallic aluminum and it is evident that, in general, the higher the percentage of metallic aluminum, the greater is the

TABLE 6.—*Aluminum and Special Deoxidation of the Eighteen Steels*

Steel	Manufacture	Al per Ton in Furnace, Lb.	Al per Ton in Ladle, Lb.	Al per Ton in Mold, Lb.	Special Treatment
H	Basic elec. arc	0.11	0.22	None	Ca-Si alloy to furnace Ca-Si alloy to furnace
I	Basic elec. arc	0.11	0.22	None	
J	Basic elec. arc	0.11	0.22	None	
K	H. F. induction	None	None	None	
L	H. F. induction	None	None	None	
M	Basic elec. arc	None	0.50	None	
N	Basic elec. arc	0.66	0.22	None	
O	Basic elec. arc	0.66	0.22	None	
P	Basic elec. arc	0.66	0.22	None	
R	H. F. induction	None	None	None	
S	Basic elec. arc	1.10	0.41	0.14	
T	Basic open hearth	None	0.93		
U	Basic open hearth	None	1.05		
V	Basic elec. arc	0.83	0.42	0.14	
W	Basic open hearth	None	0.96		
X	Electric	?	?	?	
Y	Electric	?	?	?	
Z	Electric	?	?	?	

difference in hardness between the two treatments. The apparent effect of metallic aluminum in causing graphitization when the steels have access to oxygen during tempering indicates that under this condi-

TABLE 7.—Average Hardness of Four Pre-treatments after 125 Hours at 670°C., Covered vs. Uncovered Lead
ARRANGED IN ORDER OF DECREASING METALLIC ALUMINUM

Steel	Al, Per Cent	R_b in Covered Lead	R_b in Uncovered Lead	Difference
Stable Steels				
M	0.010	91	78	13
H	0.010	91	84	7
O	0.010	88	87 ^b	1 ^b
N	0.007	89	83	6
I	0.005	89	87	2
L ^a	0.003	90	87	3
P	0.003	89	87	2
R	0.001	91	87	4
K ^a	None	91	86	5
J	None	90	87	3
Unstable Steels				
U	0.020	82	69	13
X	0.019	67	46	21
W	0.018	63	47	16
S	0.004	72	58	14
Y	0.004	50	47	3
Z	0.004	41	36	5
T	0.003	71	64	7
V	0.002	70	62	8

^a Steels K and L had Ca-Si alloy added to metal.

^b Specimen O showed marked segregation, so an average hardness is difficult to obtain.

tion the Al is oxidized to Al_2O_3 , the nature or dispersion of which is similar to that resulting from aluminum additions to the mold.

The profound effect of environment during tempering is clearly revealed in a comparison between the well-defined graphite-free spheroidized structure shown in Fig. 1 and the unetched microsection of Fig. 6. The former was taken from stable steel H tempered in covered lead for 600 hr. while the latter was photographed from a specimen of the same steel tempered for only 125 hr. in an oxidized lead bath.

As regards the steels that graphitize under either tempering treatment, it is probable that the increase in rate of graphitization in uncovered lead is due to an increase in number of alumina nuclei. The

formation of these nuclei is dependent on oxygen penetration resulting in oxidation of some of the metallic aluminum in solution in the steel. The structural difference resulting from these two conditions of tempering is illustrated by Figs. 7 and 8. These photomicrographs show, respectively, the microstructures of the unstable steel Z after heating 125 hr. at 670° in covered and in uncovered lead. The increased nucleation resulting from the formation of alumina on account of oxygen penetration, is also clearly revealed in the two macrosections of the unstable steel X at 7 dia. (Figs. 12 and 13). The difference in distribution of graphite noted in these pictures is discussed in the next section.

FURTHER COMMENTS ON ALUMINA AND GRAPHITIZATION

To the evidence submitted that the presence of alumina is an important or perhaps the chief factor in causing graphitization on tempering below the A_1 critical, the following metallographic observations may be added:

1. Macrographic and microscopic study of the distribution of the graphite particles in longitudinal sections of the unstable steels show that these particles are strung out in the direction of rolling, but the individual particles are not elongated. This characteristic obtained in steel Y after 125-hr. treatment in covered lead (Figs. 9 and 10). While the distribution of refractory alumina particles would be anticipated to be similar to that of the graphite shown in the sections illustrated, metallographic examination did not reveal any inclusions that might be responsible for graphitization. This suggests that the inclusions may be submicroscopic, or at least so minute as to render definite identification or resolution impossible by present polishing technique.

2. When the metallic aluminum content is high in a steel that graphitizes in covered lead, the observed banding effect is much less marked if the tempering treatment is

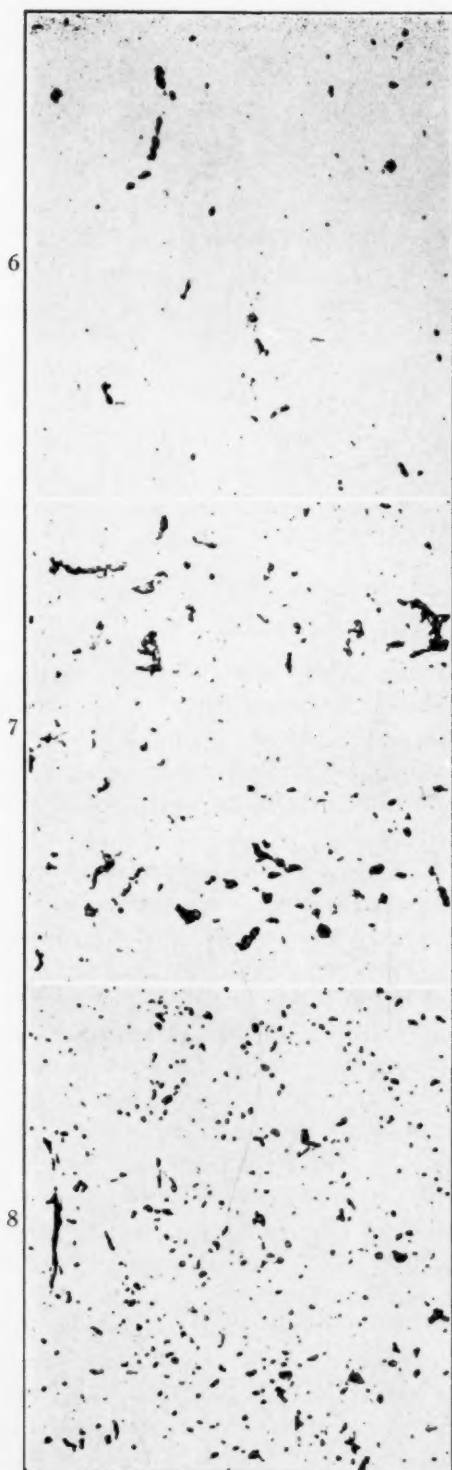


FIG. 6.—LONGITUDINAL SECTION, STEEL H.
X 200. UNETCHED.

Structure: retained graphite. Treatment: 125 hr. at 670°C. in uncovered lead. Pretreatment: 1 hr. at 1000°C. in charcoal, and water-

quenched in an oxidized lead bath. Thus steel X, containing 0.011 per cent Al_2O_3 and 0.019 per cent metallic aluminum, on treating in covered lead for 125 hr. at 670°C. exhibits the macrostructure shown in Fig. 12, whereas a similar treatment for the same steel in oxidized lead provides the macrosection illustrated in Fig. 13. The banded nature of the disposition of the graphite particles can still be discerned on close inspection of the latter figure, but the "peppering" effect due to oxygen penetration and alumina nucleation of graphite almost masks this characteristic. Furthermore, because of the large increase in the number of alumina nuclei, the growth of the graphite particles is restricted.

3. It was observed frequently that after annealing in covered lead the unstable steels were softer and more completely graphitized toward the center of the $\frac{3}{8}$ -in. dia. rods. Hardness variation has already been indicated by the data listed in Table 2. This observation would correlate with the expected segregation of alumina toward the center of the ingot.

4. During the study of the results of annealing stable steels in uncovered lead, it was noticed that with some steels graphitization to any marked extent developed only in an inner core of the sample. This characteristic is illustrated in Fig. 11, which shows a complete section of a longitudinal cut from steel O. It may be assumed that during solidification of the ingot, the metallic aluminum (0.010 per cent) present in the steel segregated toward the center of the ingot. During the 125-hr. treatment at 670°C., oxygen penetration resulted in the

quenched. Hardness: 73 to 79B.

FIG. 7.—LONGITUDINAL SECTION, STEEL Z.
X 200. UNETCHED.

Structure: retained banded graphite. Treatment: 125 hr. at 670°C. in lead covered with charcoal. Pretreatment: 1 hr. at 1000°C. in charcoal and water-quenched. Hardness: 40B.

FIG. 8.—LONGITUDINAL SECTION, STEEL Z.
X 200. UNETCHED.

Structure: retained graphite. Treatment: 125 hr. at 670°C. in uncovered lead. Pretreatment: 1 hr. at 1000°C. in charcoal and water quenched. Hardness: 32 to 36B.

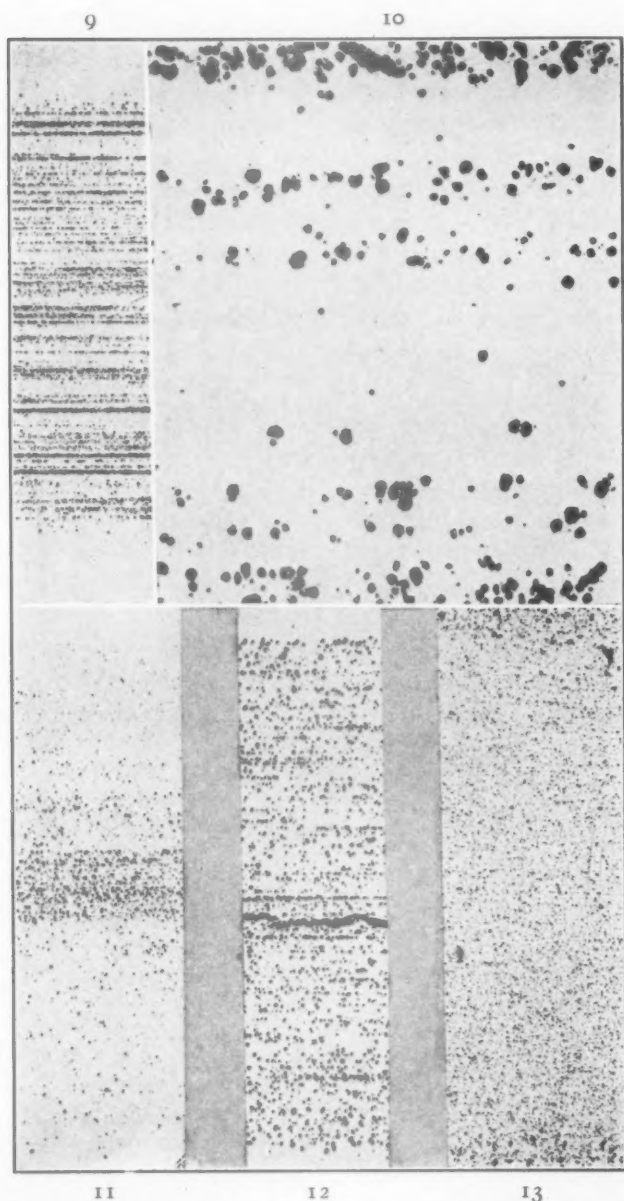


FIG. 9.—LONGITUDINAL SECTION, STEEL Y.
× 7. UNETCHED.

Structure: graphite not retained. Resulting pits show graphite distribution at low magnification. Treatment: 125 hr. at 670°C. in lead, covered with charcoal. Pretreatment: 24 hr at 850°C. in charcoal and water-quenched. Hardness: 46B.

FIG. 10.—SAME AS FIG. 9 BUT × 100.

FIG. 11.—LONGITUDINAL SECTION, STEEL O.
× 7. UNETCHED.

Structure: graphite not retained. Resulting pits show graphite segregation at low magnification. Treatment: 125 hr, at 670°C. in uncovered lead. Pretreatment: 1 hr. at 1000°C. in charcoal and water-quenched. Hardness: 81 to 89B.

FIG. 12.—LONGITUDINAL SECTION, STEEL X.
× 7. UNETCHED.

Structure: graphite not retained. Resulting pits show graphite distribution at low magnification. Also shows a quenching crack in center. Treatment: 125 hr. at 670°C. in lead covered with charcoal. Pretreatment: 1 hr. at 1000°C. in charcoal and water-quenched. Hardness: 56B.

FIG. 13.—LONGITUDINAL SECTION, STEEL X.
× 7. UNETCHED.

Structure: graphite not retained. Resulting pits show graphite distribution at low magnification. Treatment: 125 hr. at 670°C. in uncovered lead. Pretreatment: 1 hr. at 1000°C. in charcoal and water-quenched. Hardness: 38 to 44B.

formation of inoculating particles of aluminum oxide with concomitant graphitization, principally occurring in the aluminum-rich core. It is unlikely that all the metallic aluminum would segregate in the center of the ingot, and it is to be noted that limited graphitization in regions away from the core indicate that some aluminum was present in these locations. Oxidation to alumina provided some nuclei for rather meager graphitization.

SUMMARY

From a limited statistical analysis it appears that the graphitization of hyper-eutectoid carbon steels upon prolonged annealing below the A_1 is closely associated with deoxidation practice. Alumina formed during deoxidation, or produced in the steel by the oxidation of residual aluminum, when annealing is carried out in an oxidizing atmosphere, appears to be the active nucleating agent. Furthermore, the alumina must be present in the steel in a certain physical state before it is effective. These conditions are met by the alumina resulting when aluminum is added to the mold or from oxidation of the residual aluminum in the steel.

In addition to the recorded facts that more aluminum was added to the steel and that the chemical analysis for alumina was higher for the graphitizing than for the stable steels, another observation provides correlative evidence to indicate that alumina is the reagent responsible for promoting graphitization. This observation relates to certain microstructural characteristics noted in the graphite distribution in the $\frac{3}{8}$ -in. dia. rods after prolonged tempering.

Thus it is shown that the graphite is strung out in the direction of rolling, giving rise to a banded structure, and that this banded structure is obliterated or masked when annealing is carried out under an oxidizing condition, owing to the random location of the nucleating alumina particles formed by oxidation of aluminum in situ during prolonged tempering.

Regarding the other substances present in these commercial steels—carbon, manganese, silicon, sulphur, phosphorus, chromium, nickel, copper, aluminum and nitrogen, it is shown that an increase in any one of these elements, within the limits found in the carbon steels investigated, has no effect on graphitization below the A_1 . It is observed, however, that the graphitizable steels are in general low with respect to some of these elements, such as manganese, silicon, phosphorus and nitrogen. This is a further indication that steelmaking practice, especially deoxidation, is closely associated with graphitization. In this respect it is especially noteworthy that the steels highest in silicon are the most resistant to graphitization below the A_1 . It is also important that the carbon content of the graphitizable steels was somewhat on the low side, showing that graphitization is not due to differences in carbon content.

ACKNOWLEDGMENTS

The authors have pleasure in acknowledging their indebtedness to the various steel companies for the supply of selected carbon steels. Particularly do they wish to express thanks for complete general chemical analyses of the bar stock, to Mr. G. V. Luerssen (Carpenter Steel Co.) and Dr. Miles K. Smith (Latrobe Electric Steel Co.) and to Mr. Harry W. McQuaid (Republic Steel Corporation) for analyses for nitrogen, metallic aluminum, and aluminum oxide; and to Mr. J. L. Gregg (Bethlehem Steel Corporation) for analyses for oxygen by the vacuum-fusion method.

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Hydrogen Embrittlement, Internal Stress and Defects in Steel

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(New York Meeting, February 1941)

MANY hundreds of publications have appeared during the past 78 years that treat the subject of hydrogen in iron and steel,¹⁰⁵ but conclusions regarding the functions of hydrogen in causing some important defects in steel are still unsatisfactory to many; and other hydrogen-caused phenomena yet remain to be identified with this gas.

The most widely discussed of these defects is hydrogen embrittlement, but the conception, perhaps the popular one, that embrittlement is due to hydride formation does not conform to the known facts.¹⁰⁴ The true identity of hydrogen embrittlement seems instead to lie in a mosaic nature of metal crystals, which is a concept not yet accepted by most metallurgists. A study of hydrogen embrittlement therefore provides new viewpoints in regard to the crystalline substructure of steel.

A second widely discussed hydrogen-caused defect is the "flake" or "shatter crack." Although it is generally agreed that the presence of hydrogen is a prerequisite for their appearance, it is also realized that internal stress plays a decisive part. The relationship of hydrogen to internal stress has not been explained very clearly; nor is it always clear what the relationship is between a "flake" and a "snowflake," or between a "fisheye" and a "shatter crack." More importantly, the relationships

among hydrogen embrittlement, hydrogen-caused fissures such as "flakes" and the ultramicroscopic structure of steel have scarcely been recognized.

The present investigation attempts to provide an explanation for the embrittlement of steel by hydrogen by showing cause for accepting the "block" concept of metal crystals, and then to show how the numerous hydrogen-caused defects are interrelated in the light of this concept.

EVIDENCE OF SUBSTRUCTURE IN METAL CRYSTALS

It appears that the concept of a crystal as an aggregate of smaller multi-atom units must be accepted in some form if the behavior of metals is to be understood. The abundant literature on the evidence of an ultramicroscopic "mosaic" structure in metals and other crystalline substances suggests that the physicist has provided the metallurgist with an invaluable new insight. The exact picturization that any one physicist provides may be open to question, but the fact that there is some such fundamental substructure seems undeniable.

The present work makes no pretense of comprehensively treating the imperfection structure theories. Nor will conclusions be drawn here regarding the exact nature of the substructure of crystals. However, the acceptance of some imperfection theory of fundamental attributes seems so necessary to an understanding of the behavior of hydrogen in steel that the following brief

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¹⁰⁶ References are at the end of the paper.

review of evidence for a crystal substructure is presented.

One hundred and forty years ago a famous French crystallographer¹ proposed that crystals were composed of "fundamental structural units" and it is noteworthy that Henry Marion Howe pictured iron crystals as composed of unit cubes.⁵

The introduction of X-ray diffraction at the beginning of the present century gave such emphasis to the homogeneous nature of atomic configuration that the imperfection theories were quite forgotten. Darwin,^{3,4} in 1914, called attention to the fact that the intensity of X-ray reflections is much greater than could result from a homogeneous array of atoms. He proposed that the structure of crystals was a mosaic made of unit crystals that were perfect in themselves but in slight disarrangement with one another. The units, he concluded, must be less than several thousand atom diameters in dimension and need not be geometrically situated. The argument has been adjudged sound by subsequent investigators.^{23,31,47,63,79,84}

Among the early sporadic attempts to identify the substructure of metal crystals, etch pits proved popular, and, indeed, today still too little is known regarding the phenomenon of etch pits. Kaye and Ewen² many years ago produced etch pits by heating iron, and concluded that a "crystal unit," which they assumed was a fundamental structural unit, first loses molecules from its surface and then disintegrates. From the great amount of work done with etching, it is pertinent only to point out that etch figures, when produced carefully, have uniform size and regular distribution, indicating a periodic function of the metal lattice;^{31,50,58,75} and the crystallographic exactness of the pits is remarkable. Their very nature suggests an integrated structure of crystals.

Lucas^{5,15} showed that cubes about 10^{-5} cm. in size etched out of martensite and austenite; and Belaiew,⁶ polishing pearlite

lamellae at an angle to make them appear wider under the microscope, found that the edges of the lamellae were serrated, and that ferrite showed unit cubes approximately 2.5×10^{-5} cm. on an edge, whereas cementite showed unit rectangles with one dimension the same as that of the ferrite.

Tammann and Bredemeier⁷ showed that metals have a surprising submicroscopic vacuousness that permits the metal to absorb appreciable quantities of gases and liquids. This vacuousness varied with cold-working and annealing in a manner that suggests a relation to the imperfection theories under consideration. Desch,³¹ discussing the solution of crystals in liquids, stated that with the ultramicroscope it is possible to see a tiny particle leave the crystal during solution, speed through the solvent in Brownian movement and then suddenly disappear by dissolution.

Smekal^{8-10,13,25,26,37,38} has presented a strong case for the imperfection theory. His argument can be summarized as follows: Thermal expansion, optical and X-ray properties and the elastic modulus are examples of crystal properties that are "insensitive" to treatment of the crystal—that is, they seem to be characteristics of the substance and generally are invariant among specimens having different histories. The proportional limit, tensile strength, resistance to slip, diffusion; self-diffusion, thermal and electric conductivity, photoelectricity, chemical activity and crystal growth, however, are properties that depend upon the previous treatment of the crystal and therefore may be called "structure sensitive." The reactions are similar whether a single crystal or a polycrystalline material is used. Insensitive properties conform with theoretical calculations, but large errors develop in regard to the "sensitive" properties. For example, measured tensile and shear strengths of some crystalline substances are less than one per cent of the calculated, and ionic conductivity is many thousand times too small. Such discrepan-

cies can scarcely be explained save on the basis of lattice imperfection and substructure. Why, Smekal asks, do metals fail transcrystallinely if there is no imperfection structure? One experiment Smekal made with rock salt is especially interesting, wherein he showed that, during irradiation, colored sodium atoms precipitate in the disjunctions that are opened by cold-work. Other investigators have suggested that diffusion may occur through these disjunctions, for, as Rosenhain²¹ points out, it is not very reasonable to suppose that in close-packed metals diffusion proceeds by atom interchange or through lattice interstices.

The polemics between Smekal and Zwicky^{19,28,29,44} over the nature of the substructure have undoubtedly done much to defeat the whole concept in the eyes of metallurgists. Each one's denunciation of the other's argument has perhaps given metallurgists the mistaken impression that the whole argument is untenable. Such an impression is unfortunate, for a substructure probably exists. Zwicky, however, considers that the imperfections in question are geometrically arranged in the form of a "secondary structure," whereas Smekal insists that the imperfections are more or less haphazard. Whether one or the other is right is unimportant for the present purpose. The important thing is that there appears to be a substructure of some nature that is fundamental to crystallography.

Zwicky's belief in a geometrical "secondary structure" is based upon the fact that physical properties for a given treatment of the specimen do not have a wide spread through successive measurements, as would be expected if the imperfections were placed haphazardly; that the strength of a specimen varies closely with the amount of impurity present; that at elevated temperatures the slip resistance is independent of temperature until the crystal suddenly melts; and, lastly, that the concept subscribes to Fourier analysis and in general

conforms to the strict regimentation of atoms that characterizes crystals.

Evjen²⁴ has strengthened Zwicky's argument by showing that "residual rays" in deformed crystals necessitate for their explanation a geometrical arrangement of disjunctions; and Focke³² found that polonium enters nearly equally spaced cleavage planes of bismuth, the average distance between planes being 9×10^{-5} cm. Goetz and Focke^{33,34} show that crystal diamagnetism in bismuth can be explained if a periodic substructure is assumed. Andrade^{45,74} points out that the equal spacing that characterizes slip planes must have some special significance; and experiments using colloidal magnetic iron oxide on the surface of iron indicate that the block structure of ferrite is periodic and that the blocks may correspond to Weiss domains.^{46,67,76} The Barkhausen effect certainly has a resemblance to the step-wise magnetization that should result from a block structure.^{11,14,19,31,38,71,80}

In another field is shown the relation of surface imperfections to catalysis and surface reactions.^{12,17,20} Davey²³ makes the picture of imperfections sound reasonable by pointing out that surface tension on an ionized crystal, such as rock salt, would cause surface ions to pull over until every nth ion would be over a like ion, if the array were homogeneous. A periodic system of fissures would compensate for that. Maier⁵² has also discussed the subject.

Sliding of two metal surfaces over one another takes place in jerks,^{59,60,89} and the surfaces appear to have less than 0.01 per cent of their areas in actual contact. One of the most significant indications of block structure is the "survival" phenomenon³³ wherein characteristics of a given crystal are retained through short melting ranges. If melting progresses first by loosening interblock bonds, the survival phenomenon can be explained. Lastly, damping effects in metals seem to require some theory of crystal imperfection.^{82,112}

At present the best tool for resolving submicroscopic structure is the X-ray, but there are severe limitations that will have to wait perhaps for the electron microscope. Nevertheless, besides Darwin's postulate for intensity deviations, there has been work to show that Laue diffraction patterns register substructure nonuniformities;^{35,47,48,64} and "radial asterism" has been described as being due to dislocation of the mosaic structure.^{43,48,50,51,70} Line broadening and diffuseness in diffraction patterns may be due either to the mosaic structure or to lattice distortion,⁹² but Wood^{18,27,49,51,61,72,73,100} has shown that, as particles become about a micron or less in size, the X-ray pattern becomes diffuse; and he has shown that this diffuseness is more than can be accounted for by lattice distortion and hence must be due in part to a change in the conformation of the blocks.*

Goss^{48,50,57,88} has shown that as cold deformation increases, breaking the crystal into smaller units, clear diffraction patterns can still be obtained by reducing the size of the X-ray beam progressively with the degree of reduction. In this manner he has obtained a clear pattern of material cold-reduced 95 per cent. Furthermore, he has shown that the grain refinement reaches an ultimate particle size of about 10^{-5} cm., which agrees with the dimension of the crystal unit in question.

The best general picture is probably that of Gough and Wood,^{51,61} who conclude that the substructure of a crystal during deformation behaves as follows:

1. Dislocation of a normally perfect grain into components varying in tilt from 1° to about 2° from the orientation of the parent grain (probably the so-called "lineage" structure);
2. Formation of blocks between 10^{-4} and

10^{-5} cm. in size, showing wide divergence in orientation;

3. Lattice distortion within the blocks. These investigators found that with each increase in stress the substructure comes to a steady state, which again suggests that the block is fundamental to the crystal system. The sizes of blocks in several metals have been estimated by Taylor.^{41,42}

The importance of this subject is reflected in the symposium on Internal Stresses in Solids conducted by the Royal Physical Society of London during January 1940^{74,76,77,79,81,84} and by the views of numerous writers who admit that some type of substructure must exist, but do not specify its nature too closely.^{16,30,36,39,40,53,55,56,62,65,78,83,86,90,93,97,99}

RELATION OF HYDROGEN EMBRITTLEMENT TO CRYSTAL SUBSTRUCTURE

*A Theory for Embrittlement**

On the strength of the foregoing citations, it will be assumed that metallic crystals, specifically iron and steel, have some type of network of ultramicroscopic disjunctions, and that these disjunctions are part of the fundamental crystal structure. The relation of absorbed hydrogen to such disjunctions can then be directly inferred, for, under the conditions of extreme supersaturation that ordinarily characterize hydrogen in steel, each disjunction between these blocks must tend to attain its own equilibrium relations in regard to interstitially dissolved hydrogen atoms and precipitated molecules.

The researches of Moore^{57,68,69} and Smith⁹⁸ have done much to demonstrate that hydrogen absorption and occlusion are

* In the authors' opinion, the term "crystallite," used principally by English investigators, may be misleading. Until a more satisfactory name can be supplied, the word "block" will be accepted.

* It is important to understand that the "hydrogen embrittlement" under consideration in the present work is specifically the embrittlement that is caused by pure hydrogen operating within a pure iron crystal, which exhibits itself by *transcrystalline* fracture. *Intercrystalline* embrittlement, such as is found in boilers and in chambers for ammonia synthesis, is not discussed herein.

related to this rift or slip-plane structure. These investigators show that the principal portion of absorbed hydrogen in iron is contained as partially ionized molecules occluded in internal rifts, presumably of the type under discussion. Solution in the lattice must also occur, but to an extent that probably depends upon the pressure of the gas in the adjoining rift, according to known solubility laws.

The interblock disjunctions apparently may often be negligibly small, or may exist only potentially and await an imposed stress for their development. The present hypothesis for hydrogen embrittlement, substantiated by experiment, is that occluded hydrogen may provide that stress. The formation of slip lines during cold deformation in metals is known to concur with attainment of the yield stress, so it may be assumed that the block structure is elastically rigid until stressed to that limit, whereupon groups of the unit blocks become displaced and the displacement shows as a slip line. On the basis of the same reasoning, these blocks must be affected in a somewhat similar manner when the aerostatic pressure of hydrogen occluded among them exceeds the yield strength.

There is much evidence to support this hypothesis. Most of it was reviewed elsewhere¹⁰⁴ and will not be repeated here, but additional evidence will be supplied by experiment. Briefly, the effects on steel of cold deformation and hydrogen absorption are closely analogous and, when pictured from the viewpoint of the block theory, show that each process, depending upon the stress it exerts, acts to displace the blocks and to open the structure among them. Each removes the yield-point phenomenon; each affects magnetic and damping properties in the same way; each decreases the density of steel, increases the attack of steel by liquid reagents (by permitting the liquid to enter among the blocks); and, when the stress (or hydrogen)

is removed, the steel in each case retains the effects in some degree until heated to a temperature where recrystallization can occur. Such behavior indicates a block

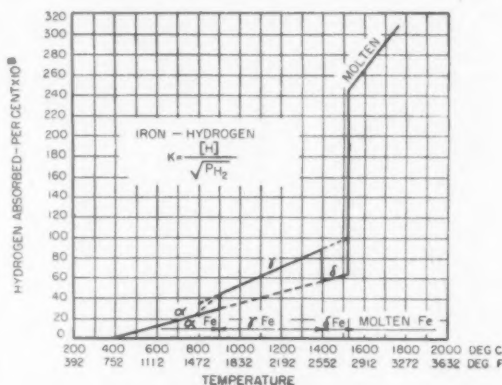


FIG. 1.—DIAGRAM (SLIGHTLY IDEALIZED) SHOWING VARIATION OF REVERSIBLE SOLUBILITY WITH TEMPERATURE FOR HYDROGEN IN IRON UNDER ONE ATMOSPHERE PRESSURE.

substructure. Of particular interest now is that X-ray diffraction lines from hydrogen-containing iron are diffuse, for such diffuseness has just been explained in connection with cold-working as being due to block displacement. Attempts to show evidence of hydride formation in iron by X-ray patterns have failed completely.

Reasons for dismissing the hydride theory for hydrogen embrittlement of iron and steel were listed in a previous publication¹⁰⁴ and will not be repeated here.

The mechanism by which hydrogen produces tremendous aerostatic pressures when trapped within steel has been discussed elsewhere^{102, 104-107} and will be restated now only to the extent of reproducing two diagrams in Figs. 1 and 2. Fig. 1 is a slightly idealized curve showing how the solubility of hydrogen in iron under one atmosphere pressure varies with temperature. The true reversible (lattice) solubility cannot be measured below about 400°C. because the block structure then becomes so prominently developed that inordinate quantities of the gas can occlude within the disjunctions. There is good reason to believe, however, that the solubility con-

tinues to decrease with decreasing temperature. Regardless of the exact shape of the curve below 400°C., it is obvious that steel after cooling to ordinary temperatures is

Fig. 2 shows the surprising curves obtained when the \sqrt{P} law is used for calculating equilibrium pressures of molecular hydrogen necessary at a lattice terminus to

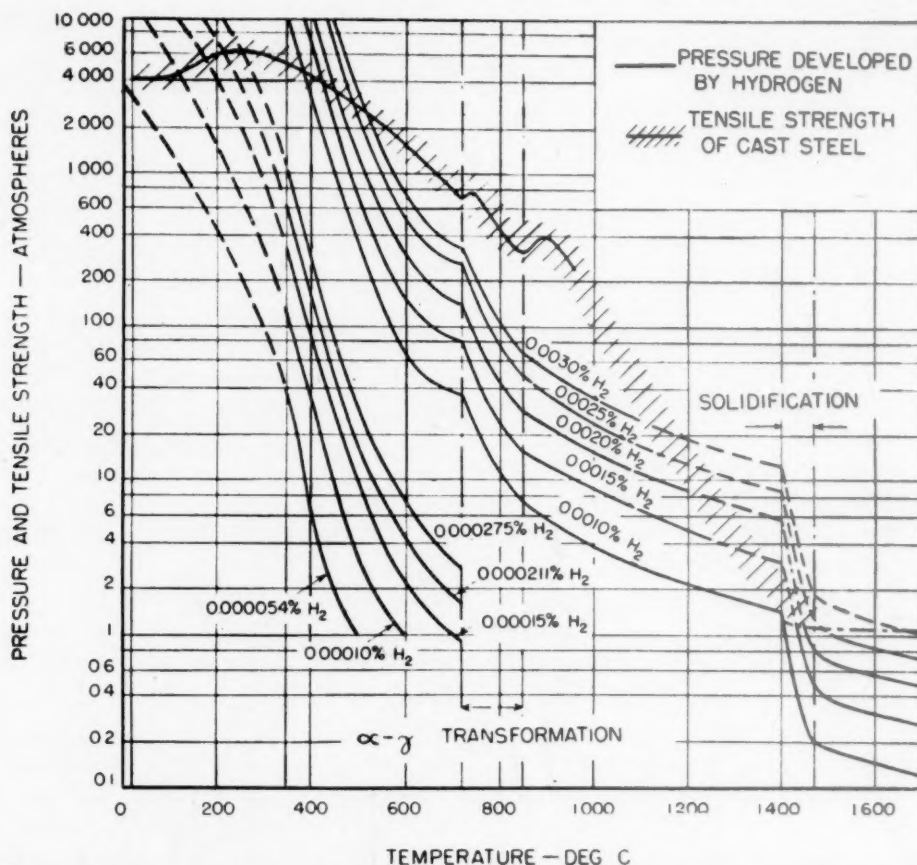


FIG. 2.—THEORETICAL VARIATION WITH TEMPERATURE FOR EQUILIBRIUM PRESSURES OF MOLECULAR HYDROGEN OCCULDED WITHIN STEELS OF VARIOUS HYDROGEN CONTENTS. (LUCKEMEYER-HASSE AND SCHENCK.)

always most amenable to supersaturation with hydrogen and consequently to internal accumulations of hydrogen under high pressure. Pickling and cathodic electrolysis can also cause great supersaturation because these processes create concentrations of atomic hydrogen on the surface of the steel that are equal to or greater than concentrations occurring in pure hydrogen at elevated temperatures. The fact that the surface concentration of hydrogen atoms is the determining factor in the solubility of this gas in steel need not be reviewed.¹⁰⁴

prevent atoms of the gas dissolved at some higher temperature from precipitating during cooling. It can be seen that normal hydrogen contents of steel, as determined by analysis, can easily supply interblock stress equivalent to that produced by cold deformation.

When the supersaturation of hydrogen in steel exceeds a certain degree, the substructure disjunctions will collect molecular hydrogen under a pressure exceeding the elastic strength,* and therefore sufficient

* The value of the aerostatic stress at which the embrittling action becomes operative has

to "spring" the blocks, or force them apart. That phenomenon, in the present view, constitutes hydrogen embrittlement of iron and steel.

The outstanding characteristic of steel embrittled by hydrogen* is that the fracture is exceedingly bright and shiny. The reflection of light from a mass of the flat

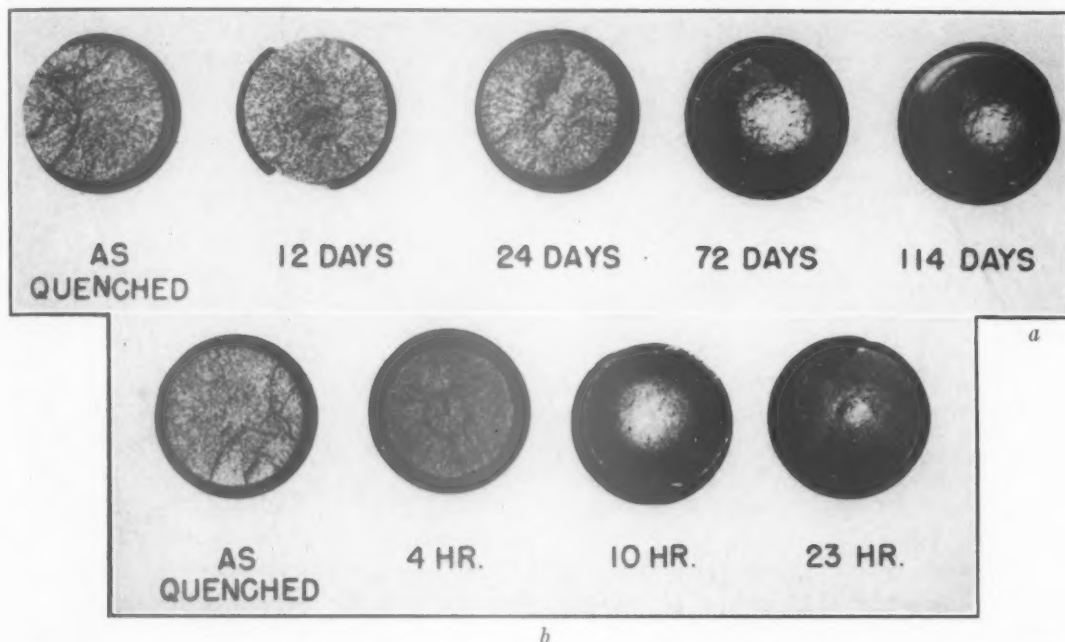


FIG. 3.—FRACTURES OF $\frac{3}{4}$ -INCH PLAIN CARBON STEEL TENSILE SPECIMENS ANNEALED TWO HOURS IN HYDROGEN AT 1100°C . FOLLOWED BY QUENCHING AND AGING AS INDICATED. Upper row, room temperature; lower row, 108°C .

Fracture of Hydrogen-embrittled Steel

The great brittleness conferred upon steel by hydrogen can now be understood in the light of this concept, for the stress in the disjunctions is *aerostatic* and is therefore *triaxial*. Materials so stressed cannot flow. They can respond to an imposed stress only by rupturing, and the rupture will proceed across the disjunctions that are most favorably oriented with the imposed stress. The resulting fracture, therefore, will expose the visibly flat facets that bound the displaced groups of blocks, and will be quite distinct from the fracture of ductile metal.

been chosen advisedly here as being equal to the elastic strength of the steel. Whatever the actual equivalent may be, it is a critical value, or values, and the term "elastic strength" will be used until the detailed crystallographic mechanism can be identified.

facets, selectively oriented as they would be at right angles to the imposed stress, can account for that brightness.

In Fig. 3 is shown a series of round bars of mild steel heated in hydrogen for 2 hr. at 1100°C . and subsequently quenched and aged. The bright fracture and brittle nature of the as-quenched specimen is an indication that the decrease in solubility from 1100°C . to room temperature is sufficient to cause interblock occlusion of the gas under pressures that exceed the elastic strength of the steel. (A control specimen similarly quenched but containing no hydrogen showed no bright fracture.) Annealed in hydrogen at some lower temperature, or for a shorter period of time, or cooled more slowly, the bars would not develop embrittlement because the equilibrium pressure of molecular hydrogen

Refer to footnote on page 228.

at room temperature necessary to balance that smaller quantity of dissolved gas would be insufficient to develop hyperelastic stress among the blocks. Behavior of the

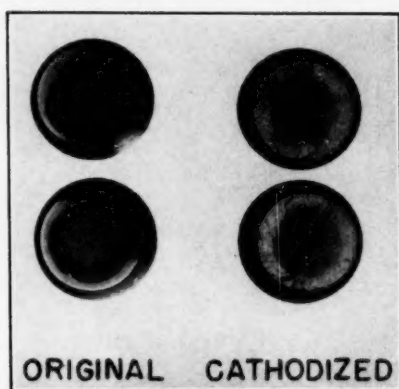


FIG. 4.—HALF-INCH PLAIN CARBON STEEL TENSILE SPECIMEN FRACTURED AFTER ONE HOUR'S CATHODIC ELECTROLYSIS.

physical properties in this type of test is discussed later.

Aging at room temperature and at 108°C. permitted slow escape of the gas with coincident return of ductility, as evidenced by the fractures. Such escape can be afforded through two processes: (1) the high pressure of the occluded gas causes re-solution of the hydrogen as atoms according to the \sqrt{P} law, with subsequent diffusion through the lattice; and (2) the fact that the substructure is forced open by the aerostatic pressure permits some of the gas to leave the steel as molecules passing through rifts that communicate with the surface.

The bars in Fig. 3 show by the retreating embrittled zone how the hydrogen concentration drops from center to rim during aging. In Fig. 4 the opposite movement is depicted by a similar bar loaded with hydrogen by electrolysis and fractured before the high-pressure zone had reached the center. Note how sharply the embrittled zone is delimited. This unique behavior of hydrogen in the substructure of the iron crystal makes it possible to detect and to follow the course of damaging quantities of hydrogen in steel.

In the following work, use will be made of the appearance of fractures to demonstrate the simple relationships that exist among the numerous hydrogen-caused defects.

"SNOWFLAKES," "FISHEYES" AND "WHITE SPOTS"

"Snowflakes" and Hydrogen Embrittlement

Redundancy of terms in the literature has been principally responsible for the fact that so many hydrogen-caused defects in steel have remained unrecognized or unsatisfactorily explained. Prominent among these stand "fisheyes," "snake eyes," "birdeyes" and "rosettes" in welding;¹⁰⁶ "flakes," "snowflakes" and "silver streaks" in forged steel and "white spots" in cast steel. Then again, there are "flakes" and "shatter cracks."¹⁰⁴ All may be caused by hydrogen and all are simple expressions of the hydrogen embrittlement just discussed, but the greatest ambiguity and confusion have surrounded the whole group. Because the two defects last mentioned relate specifically to fissuring phenomena, in contrast to the others, they will be discussed separately later.

An excellent example of snowflakes in a tensile specimen of alloy steel is shown in Fig. 5. The resemblance of the bright defaced areas to the embrittlement in the previous figures is pronounced. Snowflakes conform to the known facts regarding hydrogen embrittlement, decreasing the ductility without appreciably affecting the tensile strength and showing the characteristic bright fracture which disappears on aging or annealing. Under the microscope the snowflake is a myriad of tiny, flat, reflecting facets. Plainly, this defect is merely localized hydrogen embrittlement. If more gas were supplied to the steel, as by cathodic electrolysis, the area covered by the bright fracture would increase as in the previous Fig. 4 and, as aging progressed, the areas would decrease as in Fig. 3. The hydrogen, obeying ordinary diffusion laws, leaves

centers of highest concentration last, and careful examination of a snowflaked region will always show some central discontinuity, whether it be a slag particle, a

sions, however, are determined entirely by the shape of the occluding locus; and its size by the pressure and quantity of the gas therein, as will be described shortly. For

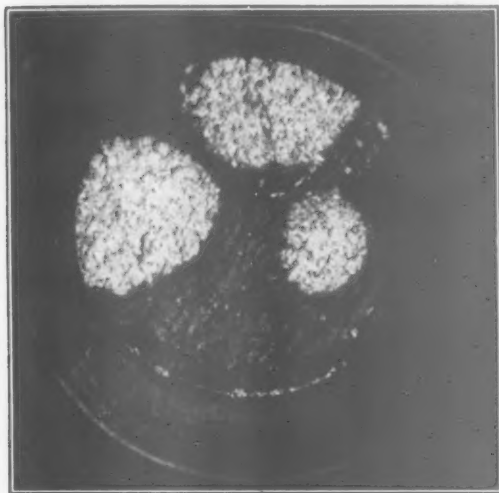


FIG. 5.—“SNOWFLAKES” IN TENSILE FRACTURE OF ALLOY STEEL. $\times 3$.

blowhole, a microshrinkage cavity or a small fissure. Because the fractured face represents only a two-dimensional cross section of an embrittled *region*, that dis-

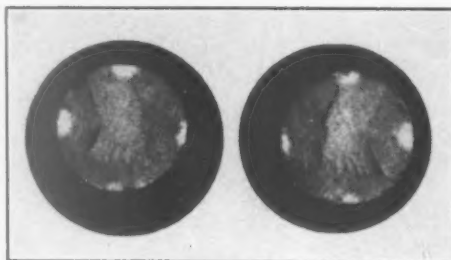


FIG. 6.—“SNOWFLAKES” ARTIFICIALLY PRODUCED BY CATHODICALLY TREATING A STEEL TENSILE SPECIMEN ONLY ALONG THIN LONGITUDINAL LINES AT QUADRANT POSITIONS.

example, “silver streaks” is the same defect occurring in rolled or forged steel where a layer-like structure occludes the gas and provides a narrow embrittled zone extending a short distance to each side of the laminated impurities.

The defect in Fig. 5 can be simulated artificially as shown in Fig. 6. An ordinary steel tensile specimen was coated with

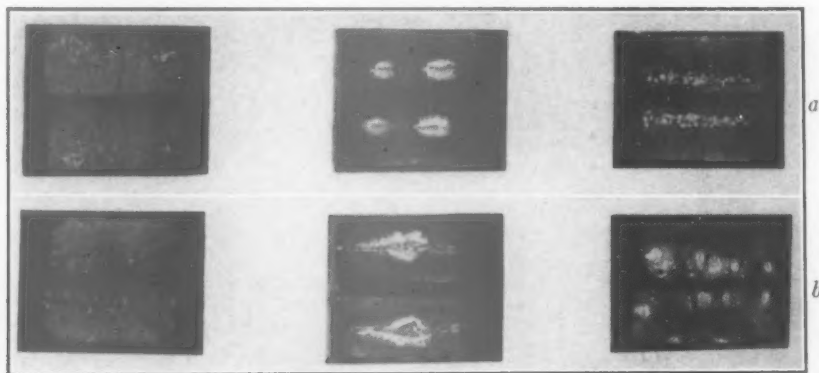


FIG. 7.—TENSILE FRACTURES THROUGH WELD METAL SHOWING THREE TYPES OF HYDROGEN EMBRITTLEMENT.

Left, embrittled throughout; center, collapsed brittle zone along disjunction of a two-bead weld; right, “fisheyes.”

continuity need not be on the fractured face, as is erroneously expected by some investigators. The embrittled zone extends well below the surface of the fracture and in unworked material is spheroidal. Its dimen-

Glyptal and longitudinal stripes only $\frac{1}{16}$ in. wide were cut through the resin at 90° positions, exposing the steel. The specimen was then made cathode in an electrolytic cell for one hour and was pulled

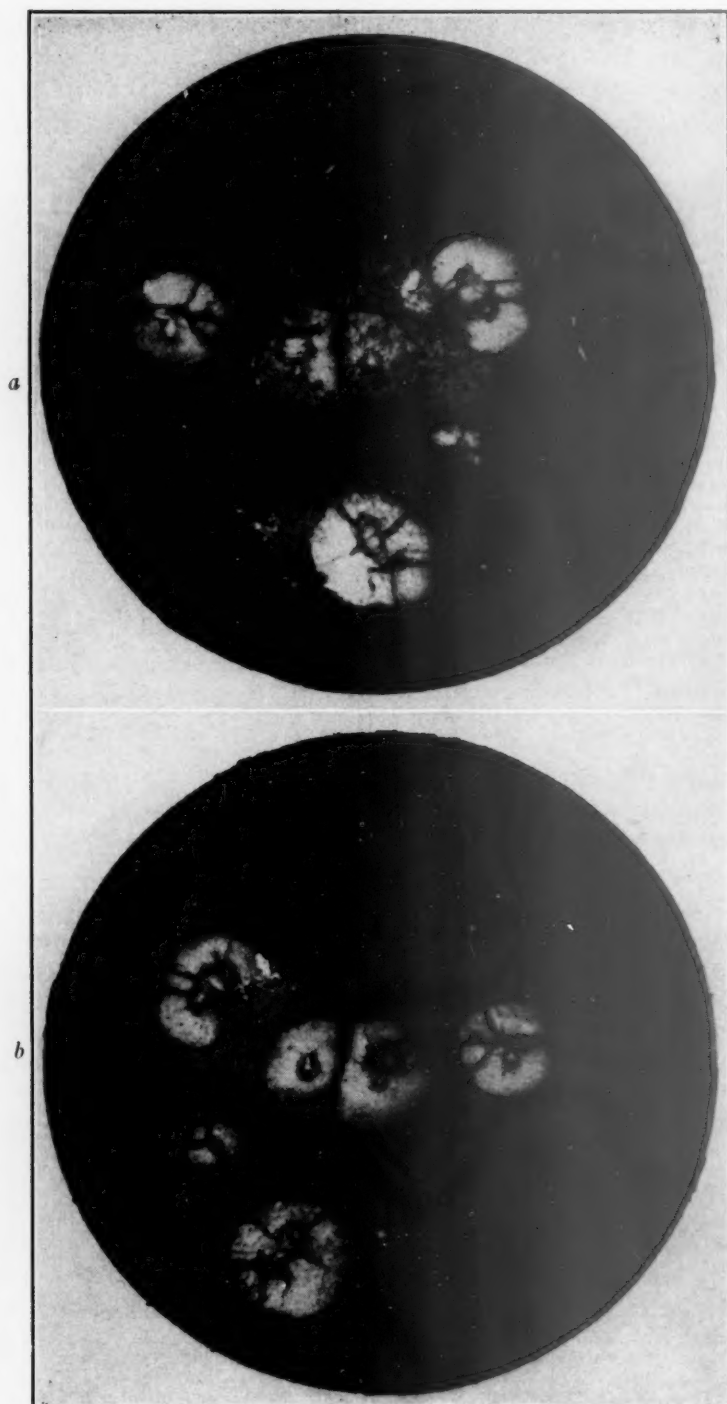


FIG. 8.—“FISHEYES” IN TENSILE FRACTURE OF WELD METAL. $\times 3$.

in tension. The fracture showed four symmetrically placed snowflakes.

"Fisheyes" and "White Spots"

Localization of hydrogen in steel specimens can assume various interesting

temperature. The hydrogen-embrittled zone accordingly had collapsed through gradual removal of the gas until only a narrow vein of brittle metal was left along the boundary of the interbead disjunction. The specimens on the right were of the "fisheye"

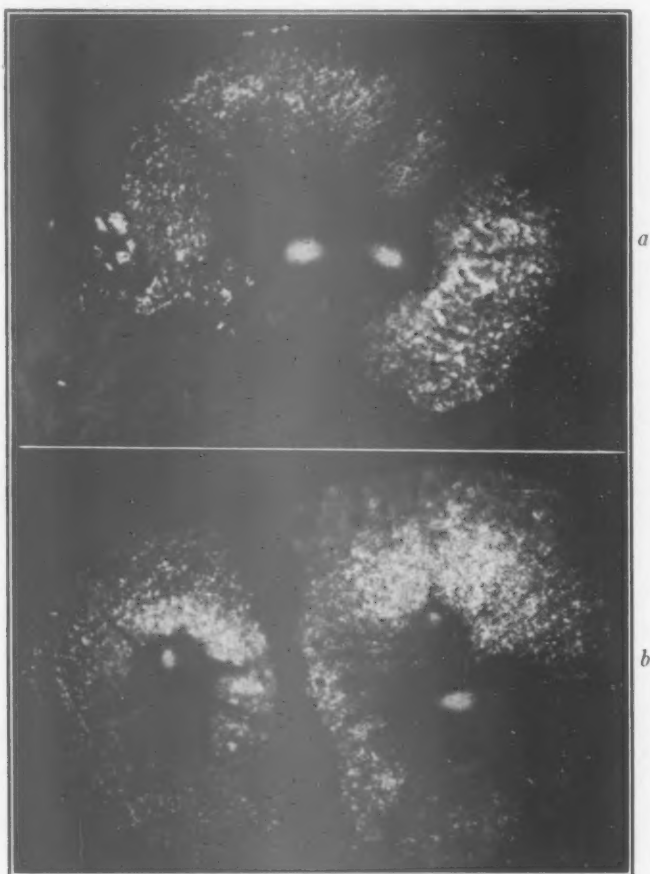


FIG. 9.—MAGNIFICATION OF "FISHEYES" IN PREVIOUS FIGURE. $\times 15$.

visual forms on fractured faces, which often have been classed as separate defects. Welders are acquainted with an abundant evidence of the effects of hydrogen in steel.¹⁰⁶ Fig. 7 shows some typical fractures through weld metal, illustrating three sets of conditions. The specimens on the left contained so much hydrogen that the entire section of each was just one large snowflake and was embrittled throughout. The central specimens were of the silver streak type and represented a two-bead weld that had aged for two weeks at room

type, and represented small zones of hydrogen embrittlement that had collapsed around numerous small inclusions or blowholes. Such a specimen generally results from moisture being present during welding and may contain surprising amounts of hydrogen because the trapping loci are often macroscopic in size.¹⁰⁶

Fig. 8 shows an excellent example of the defect variously called "fisheyes," "snake eyes," "birdeyes" or "rosettes" by welders and "white spots" by foundrymen working with cast steel. In this specimen the

occluding centers can be clearly seen without magnification, and in the enlarged view in Fig. 9 the silvery lining of the blow-hole attests the presence of a reducing gas such as hydrogen.

erupt through the surrounding metal and thereby develop an apparently brittle fracture.

The present embrittlement picture appears more satisfactory. Hydrogen under

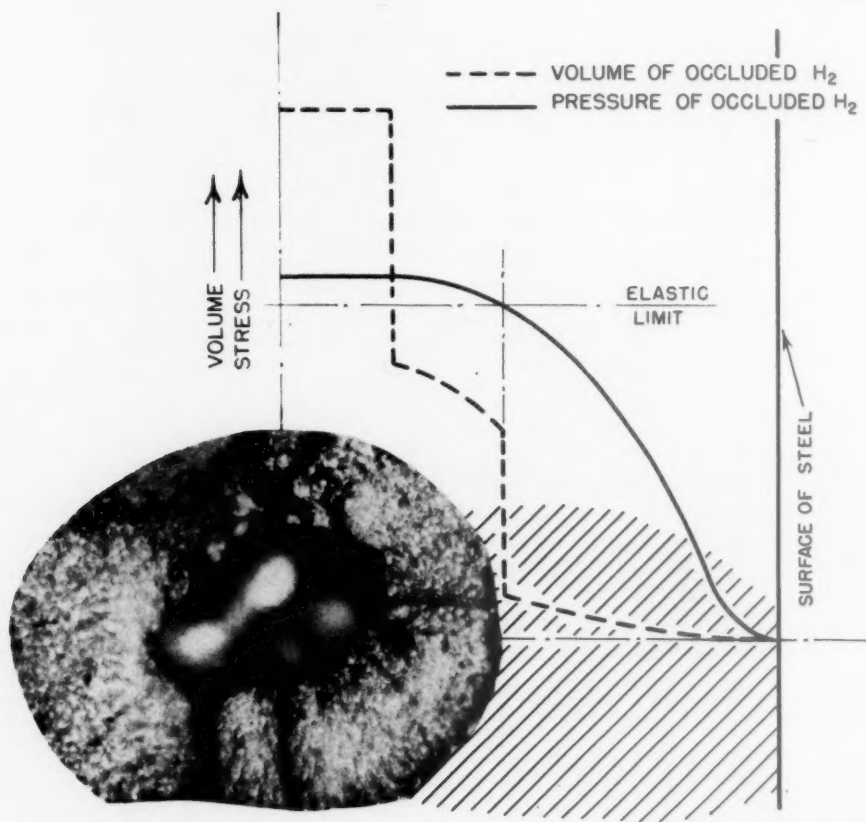


FIG. 10.—SCHEMATIC REPRESENTATION OF PRESSURE AND VOLUME RELATIONS OF HYDROGEN IN A "FISHEYE."

The phenomenon shown in these last two figures deserves particular attention. The fact that the embrittled zone is so obviously built around a gas pocket and that its boundaries are so sharply defined seems to corroborate in a striking way the theories that have been presented for the formation of these defects. Some of those who have in the past few years accepted the fact that hydrogen is necessary to flaking, have done so with some lack of conviction because it was not too reasonable that the gas gathered in an opening inside the steel under sufficient pressure to suddenly

high compression in a macroscopic disjunction must also be under high compression in all surrounding disjunctions, regardless of their size, because the gas under those pressures is free to move through the steel: (1) atomically through the lattice and (2) molecularly through adjoining rifts, as already stated.

Fig. 10 therefore has been drawn to show schematically the probable nature of these defects. The aerostatic pressure within the macroscopic cavity must be a maximum, and on the surface of the specimen, of course, the pressure must be a minimum.

There must then be some midway point where the pressure is just equal to the elastic strength of the metal, and that point must be the outer edge of the embrittled area. All metal lying between that equistress point and the occluding locus would then be embrittled, and the metal to the other side would be transferring hydrogen to the surface under pressures that were progressively less as the surface was approached.

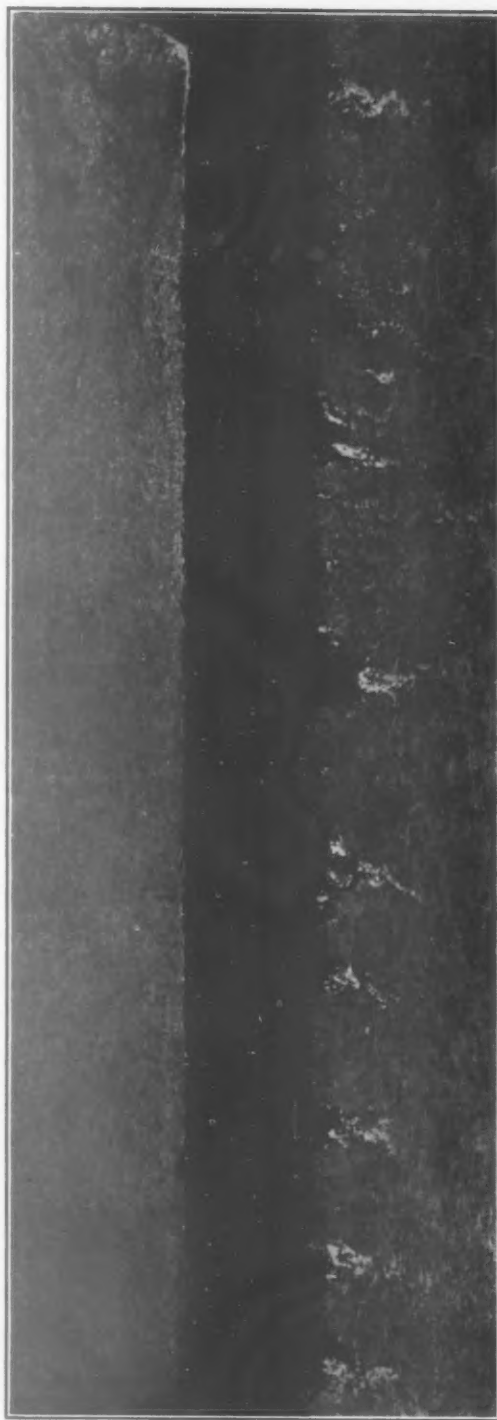
Superimposed on the sketch in Fig. 10 is a curve showing schematically how the gas content probably varies over this range. The sharp drop at the edge of the embrittled zone is based upon the reasoning that the rifts probably enlarge suddenly only when the elastic strength is exceeded, and are otherwise much smaller in volume. This is borne out by the known effects of cold-working and indirectly by somewhat analogous findings by Smith for the α and β phases in palladium.⁹⁸ That the volume decreases in passing from the cavity to the metal is probably correct for iron.

An interesting commentary here is that the pressures postulated in the present treatment of embrittlement require that each interblock rift in the brittle zone contains several thousand times its own volume of hydrogen, measured under standard conditions. The innate porosity of steel measured by Tammann and Bredemeier⁷ plus the volume increase known to occur when steel is loaded with hydrogen amounts to roughly one per cent of the total volume of the steel, and a simple calculation then shows that steel embrittled throughout should contain in the order of 25 relative volumes of hydrogen—a figure that is borne out by experimental findings.⁶⁹

EFFECTS OF SUPERIMPOSED STRESS ON STEEL EMBRITTLED BY HYDROGEN

"Checks" and "Tears"

Triaxially stressed by the aerostatic pressure of hydrogen occluded in a finely disseminated rift system, hydrogen-em-



Normal Charged with Hydrogen
FIG. 11.—EDGES OF TWO PLAIN CARBON
STEEL SHEETS, ONE CONTAINING EXCESSIVE
HYDROGEN, AFTER COLD-ROLLING. $\times 3$.

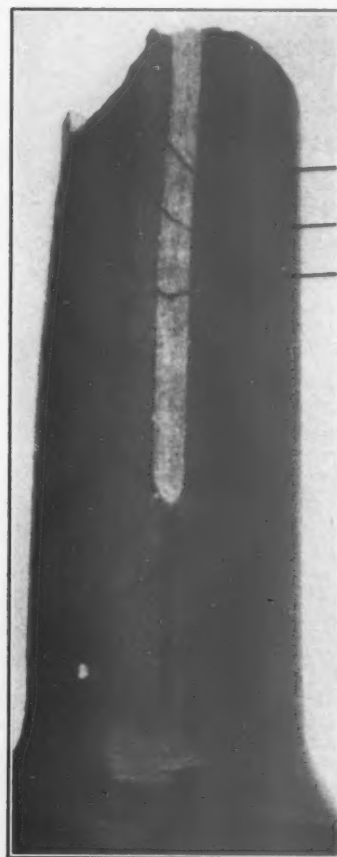
brittled metal cannot flow, as already stated, but can respond to imposed stress only by rupturing. An example of the behavior of such metal to superimposed stress is shown in Fig. 11. Two plain

carbon steel sheets were annealed $\frac{1}{2}$ hr. at 950°C ., one in hydrogen atmosphere and one in normal atmosphere. Both were then quenched, sandblasted and cold-rolled to 50 per cent reduction. The plate containing hydrogen cracked badly along the edges, as shown, and the fissures were shiny, connoting hydrogen embrittlement.

A common occurrence of this action appears in testing tensile specimens. Small "checks" or "tears" frequently appear along the side of the specimen during testing (Fig. 12a). Microexamination has so often shown slag stringers or blowholes underlying these defects that it has been generally assumed that such discontinuities concentrate stresses in a manner that lends apparent embrittlement to the outlying metal. The discontinuity, how-



a



b

FIG. 12.—SIDE VIEW OF TENSILE SPECIMENS SHOWING "CHECKS" OR "TEARS."
Left, ordinary specimen; right, artificial "tears" on specimen in Fig. 6.

ever, usually is merely an accomplice, for the tearing is more often due to embrittlement caused by hydrogen that has precipitated under pressure in that discontinuity and throughout the adjacent metal. If carefully aged or annealed to remove the hydrogen, such defects do not occur except, perhaps, in some unusual cases that are irrelevant to the present argument. When the fracture occurs across the discontinuity, the hydrogen embrittlement surrounding that locus is most evident. The specimen in Fig. 12 contained a slag stringer that was unusually long and had collected hydrogen throughout its entire length.

Tears can be produced at will by selectively embrittling with hydrogen small areas on a tensile specimen. Fig. 12 (right) shows the side view of the test bar previously described in discussion of Fig. 6. The specimen showed good ductility except along the four stripes of hydrogen-treated surface where embrittlement precluded flow and fissures formed to accommodate the stress. Thus "tears" and "snowflakes" are merely longitudinal and horizontal manifestations, respectively, of the same defect—hydrogen embrittlement.

Interdendritic Shrinkage

The cracking observed in the foregoing experiments was caused by externally applied stress. There are also internal stresses from various sources that are capable of doing the same thing, and these are often more important because they are less easily observed and controlled.

One type of internal stress results from the shrinkage that occurs when a metal solidifies. Primary dendrites form in the liquid, and as they grow together they include the remanent liquid among them. When this liquid solidifies it produces a volume of metal between the dendrites that is insufficient to fill the space formerly occupied by the liquid and the structure there is likely to be under pronounced

stress. If, during the solidification, an appreciable quantity of hydrogen is present, this gas will proceed to these interdendritic interstices along with the rest of

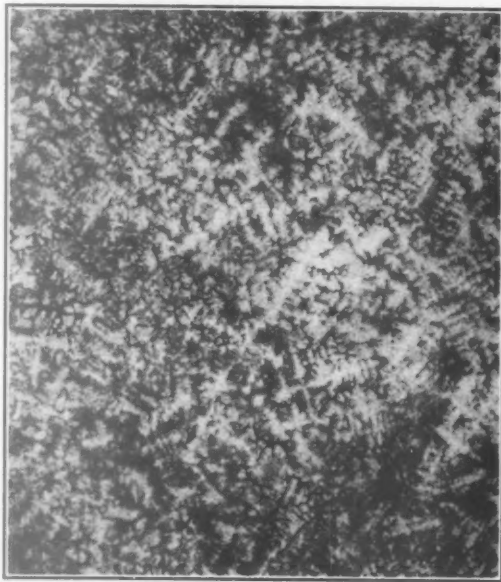


FIG. 13.—INTERDENDRITIC FISSURES CAUSED BY HYDROGEN ABSORBED DURING MELTING. $\times 5$.

the impurities—and more rapidly, because it is so readily diffusible. Embrittlement ensues and the stresses, probably aggravated by the pressure of the hydrogen in the interstices, are relieved by cracking.

The action can be demonstrated by experiment (Fig. 13). Two low-alloy steel melts were made, identical in composition except that one was made in vacuo and the other in hydrogen under one atmosphere pressure. The hydrogen-containing ingot was badly fissured throughout the interdendritic interstices, whereas the hydrogen-free ingot showed no cracks even on deep etching.

MECHANISM OF "FLAKE" AND "SHATTER CRACK" FORMATION

Relation between "Flakes" and "Snowflakes"

Among the most important defects in the metallurgy of steel is the internal

fissure known as a "flake" or a "shatter crack."*¹⁰⁴ This defect has been the cause of innumerable investigations since it first attracted major attention in the manufacture of gun forgings during the 1918 war period.

It is now generally admitted that flakes depend upon the presence of hydrogen for their formation, but the role of the gas is not clear. Nor has the relation of internal stress been clearly defined. Among the many questions that still arise are the following: When, why and how does the fissure form? Why does not the defect occur in low-carbon steels? What are the distinctions among "flakes," "shatter cracks" and "snowflakes"? Why do snowflakes sometimes reappear after they have been removed by annealing? What is the relationship between internal stress and the occluded hydrogen?

The answer to these questions follows from the reasoning established in the previous paragraphs. Thus, hydrogen embrittlement, caused by accumulation of the gas at some discontinuity within the forging or the rail, is the seat for the defect, and some superimposed internal stress operating across this brittle zone is the cause of the fissure.

The relation between the flake and the snowflake is obvious, for in a flake the embrittled zone is fissured by internal stresses developed during cooling; whereas the snowflake, for lack of sufficient internal stress, first forms when some external stress is applied, as during testing. Both defects show the same general type of fracture and are identical in nature, so that it is unnecessary to distinguish between them unless it is desirable to classify such defects according to the stage of working at which the superimposed stresses in conjunction

with the embrittlement become sufficient to cause fissuring. Minor differences in the appearance of the defect from steel to steel are due to differences in the steel.

Time and Temperature at Which Flakes Form

In the annals on these defects may be found claims for almost a separate period of formation of the fissure for each investigation. The fact seems to be that flaking, which in the present sense implies fissuring, may occur almost any time after the commencement of cooling from forging until some time years later. Enamelers have a most troublesome defect of a similar nature called "delayed fishscaling," which is caused by hydrogen precipitation underneath the enamel^{101,105,109,111} instead of within an internal cavity, as in flaking. Development of sufficient pressure to chip the enamel may take a period of years in some cases. Both the development of internal stress and the collection of hydrogen under pressure depend upon diffusion or transformation processes, which are slow at ordinary temperatures, so that an incubation period of some duration is always necessary. With increasing amounts of hydrogen that period may be shortened because the steel becomes brittle more quickly and more completely and fissuring occurs with less provocation; and the greater the internal shifting necessitated by shrinkage, thermal and transformation stresses, and the lower the temperature at which these stresses develop, the less hydrogen is necessary for embrittling the metal extensively enough so that it cannot accommodate that movement without fissuring. The strong relationship of carbon and alloy content is then obvious, for steels with these components show maximum volume change on cooling and the change occurs at lower temperatures.

The work of Cramer, Musatti and Reggiori and others¹⁰⁴ has shown that to produce flakes by annealing in hydrogen

* "Flakes" and "shatter cracks" are synonymous, the two terms having originated in the forge shop and the rail mill, respectively. In this discussion the defect will be called a flake.

some minimum temperature and time of soaking are required. The reason can be found in the curves in Fig. 2, and requires some minimum decrease in solubility to occur so that the equilibrium pressure of molecular hydrogen in internal rifts necessary to maintain the solution of atoms in the adjoining lattice will exceed the elastic strength of the steel. That pressure is of the order of several thousand atmospheres; therefore, the steel must be cooled over a range of temperature that allows a decrease in solubility, roughly, of fiftyfold. It can then be understood (refer to Fig. 1) why in commercial practice flaking generally occurs in a temperature range around 100° or 200°C. Ordinary hydrogen contents of steel may vary widely along the upper portion of the solubility curve, but they will nevertheless first obtain the fiftyfold decrease within some rather limited range of temperature below 400°C. Extrapolating the curve in Fig. 1, one can estimate that that range would be the one ordinarily observed commercially. Sudden decreases in hydrogen diffusibility around 200°C., believed by some investigators to cause the defect, are not necessary, but may be of minor importance.

Further evidence that flaking depends on the solubility decrease of hydrogen is afforded by practical observations published by Foley.⁸⁵ He reports that large forgings in an annealing furnace showed top and bottom temperatures of approximately 1200° and 1400°C., respectively. The bottoms of the ingots showed flakes, whereas the tops were flake-free and, when a temperature maximum of 1150°C. was maintained, no flakes occurred throughout the ingot. The explanation is that an unevenly heated ingot will tend to show a variation in hydrogen content that follows the temperature gradient, according to the curve in Fig. 1. The gas will leave the cooler end of the ingot, but the hot end may retain enough to permit flaking to occur. That the gas is strongly retained by

the steel at elevated temperatures will be demonstrated shortly by experiment.

It is a common experience in railmaking that flakes do not occur within $\frac{1}{2}$ to $\frac{3}{4}$ in. of the hot saw. The reason, substantiated by the following experiments, is that sufficient hydrogen is probably lost through the cut surface to obviate flaking. That the gas diffuses much more readily in the rolling direction has been established in another research.^{102,105} From the results of the present work it must be presumed that flakes would occur right up to the saw cut if sufficient hydrogen were present and the rail were cooled rapidly enough.

Experimental Illustrations of the Flaking Mechanism

Very little will be said in the present work about the genesis and the quantitative aspects of the stresses that cause the defects in question, because the subject of internal stress has been adequately covered by others. The relative importance of the various stresses from the standpoint of flaking, however, warrants some consideration.

Because railroad rails are especially amenable to flaking, rail steel is good material with which to experiment. Through courtesy of R. E. Cramer, at the University of Illinois, some sections of 131-lb. rail were obtained, which were of the same type as those discussed by Cramer in numerous papers.^{54,66,91} The carbon content was about 0.70 per cent.

Transverse and longitudinal sections (Fig. 14) through this steel revealed numerous slag stringers, which are common agents in the nucleation of hydrogen-embrittled zones that later lead to flaking.

A flat section through the head of one of Cramer's rails containing hydrogen is shown in Fig. 15. The head was used because it represents the thickest section of the rail and therefore is most prone to flaking. Important to note is that the flakes lie principally in the rolling direction

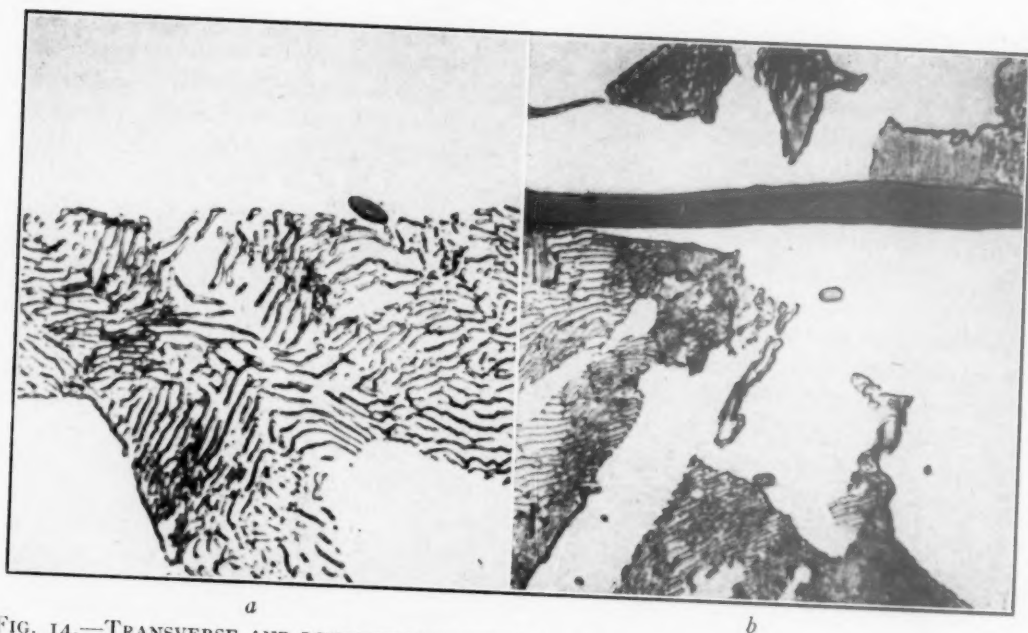


FIG. 14.—TRANSVERSE AND LONGITUDINAL VIEWS OF TYPICAL SLAG STRINGERS IN SLOW-COOLED RAIL STEEL. $\times 1000$.
Decarburized zone near surface.



FIG. 15.—HORIZONTAL SECTION THROUGH HEAD OF FLAKY CRAMER RAIL.

—only a few transversely. From this it can be concluded that rim-core stresses, at least in this specimen, are more important than longitudinal stresses in causing

embrittlement surrounds the elongated discontinuities, as expected.

The beneficial effects of slow cooling for prevention of flakes is well known and in

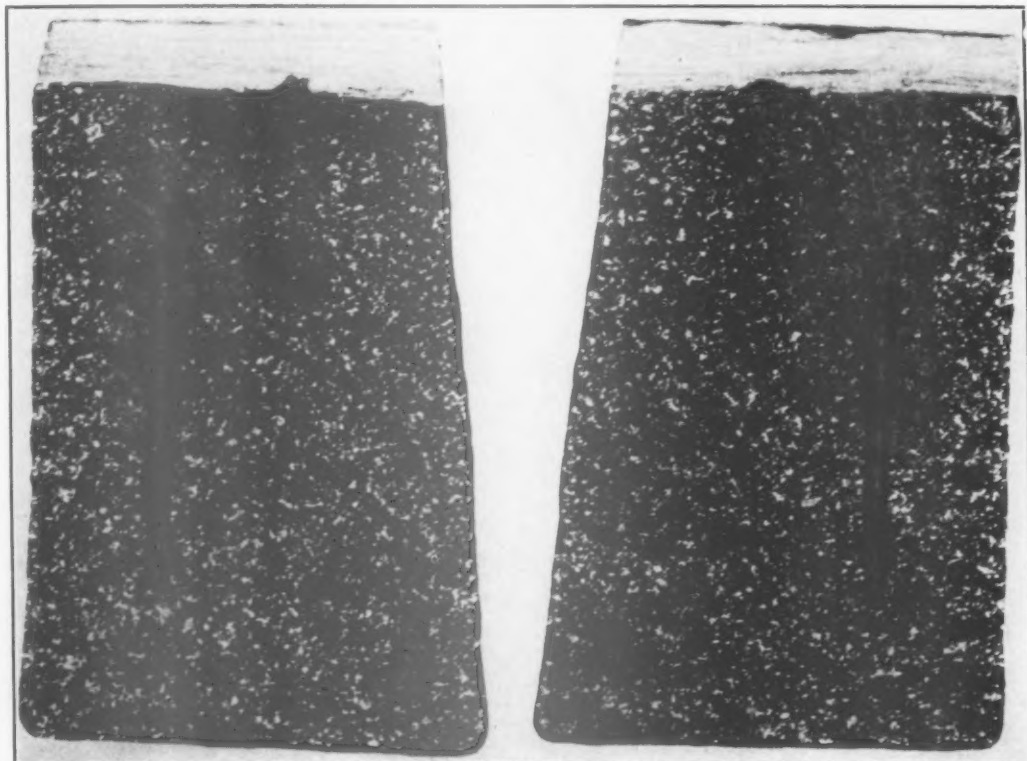


FIG. 16.—SECTION OF SPECIMEN IN PREVIOUS FIGURE FRACTURED IN ROLLING DIRECTION TO SHOW "FEATHERY" STRUCTURE OF HYDROGEN-EMBRITTLED ZONE.

flaking. The flow structure has been made especially pronounced during etching by the action of hydrogen, as will soon be explained.

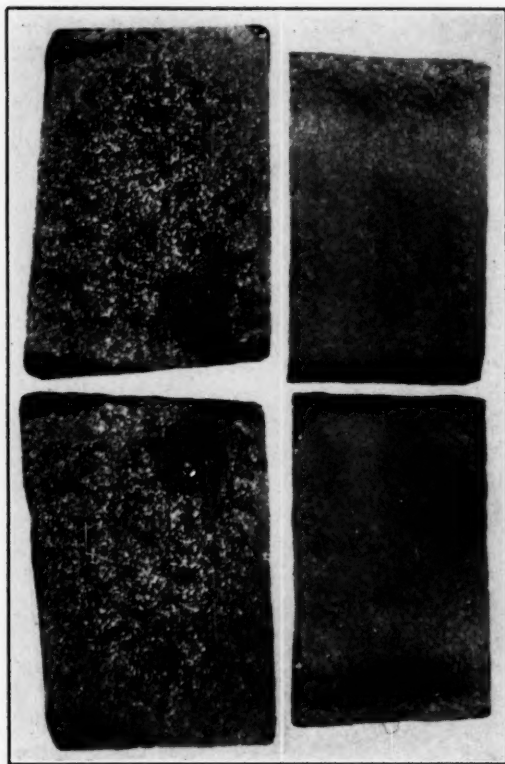
Fractured longitudinally along one of these flakes, this rail revealed the "feathery" structure shown in Fig. 16. The "feather" is a hydrogen-embrittled zone nucleated by some rolling discontinuity, such as a slag stringer, but does not show its true brightness because the fracture of the surrounding high-carbon steel is so bright. Normalized to give a fibrous fracture, similar specimens appeared as in Fig. 17. The hydrogen-embrittled metal is now more evident and it is seen that the

commercial practice the defect has its greatest occurrence in steels cooled in air too rapidly. If the steel were quenched, a minimum of hydrogen would be lost during cooling and a maximum internal stress would develop. Quenched specimens containing hydrogen should therefore develop most severe flake formation.

Head sections of 131-lb. rail were accordingly annealed for 7 hr. in hydrogen at 1100°C . and immediately quenched. A similar group was annealed in hydrogen for 7 hr. at 1200°C ., to test the validity of the assumption made earlier that the severity of flaking is proportional to the quantity of hydrogen absorbed and that that quantity generally follows the curve

in Fig. 1. Of course, internal stresses may also be greater in the specimen quenched

$\frac{1}{4}$ in. of the end, which corroborates the statement made previously that, commer-



Containing Hydrogen Hydrogen-free
FIG. 17.—SECTIONS SIMILAR TO THAT IN FIG. 16 NORMALIZED BEFORE FRACTURING TO SHOW HYDROGEN EMBRITTLEMENT.

from the higher temperature. Flat sections of a rail from each group are shown in Fig. 18, and it is evident that the higher temperature has greatly increased flaking.

The severity of the flaking is remarkable. All sizes from microscopic fissures to a major transverse crack have developed. The dispersion and directions of the flakes graphically illustrate the mechanism of flaking, for the whole specimen was embrittled throughout with hydrogen and each significant stress caused fissuring. Perpendiculars drawn to the flakes in this photograph would very nicely depict the internal stresses that developed in these specimens during quenching.

In the specimen quenched from 1200°C . large transverse flakes appeared even within

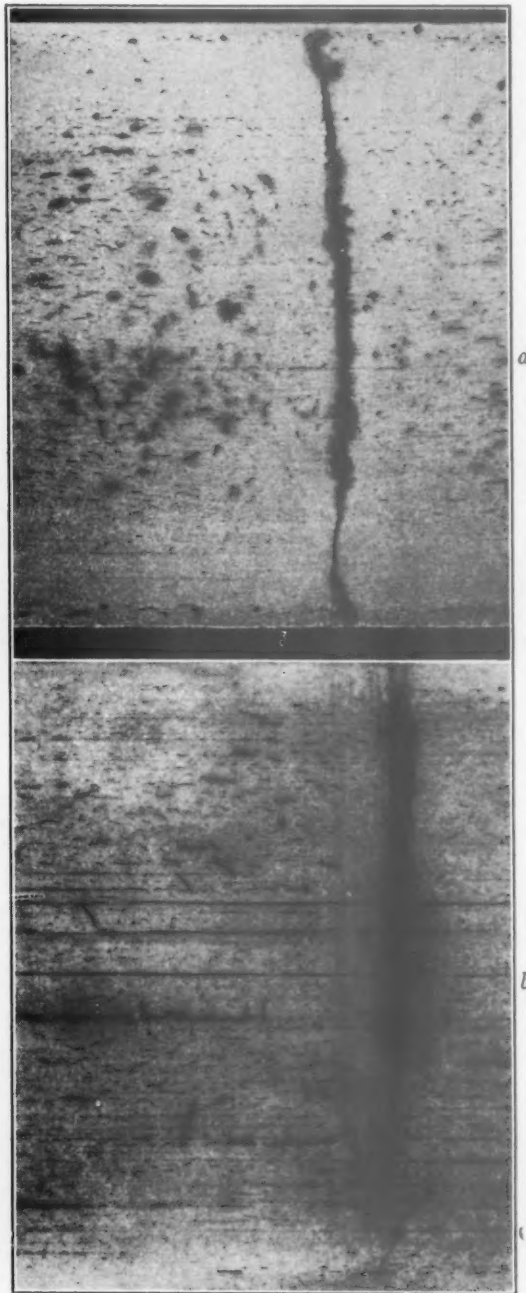


FIG. 18.—HORIZONTAL SECTIONS OF RAILHEADS ANNEALED IN HYDROGEN FOR SEVEN HOURS AND QUENCHED.

a, annealed at 1100°C .; *b*, annealed at 1200°C .

cially, flakes do not occur within about $\frac{1}{2}$ in. of the hot saw because sufficient hydro-

gen is not present. Even the decarburized rims in the present specimens were separated from the parent material by fissures.

steel and was then broken through the major transverse crack. Fig. 19 shows that the crack (black oxidized area) had almost

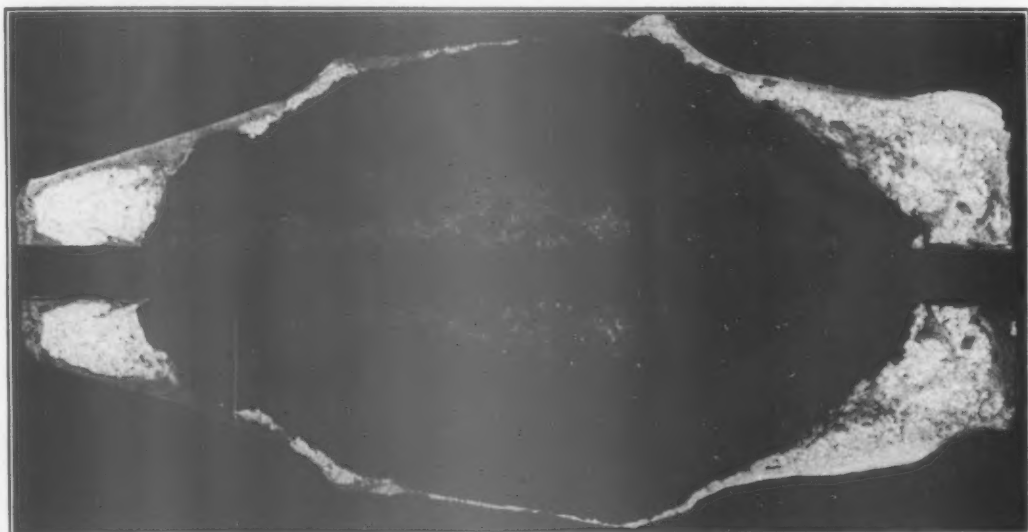
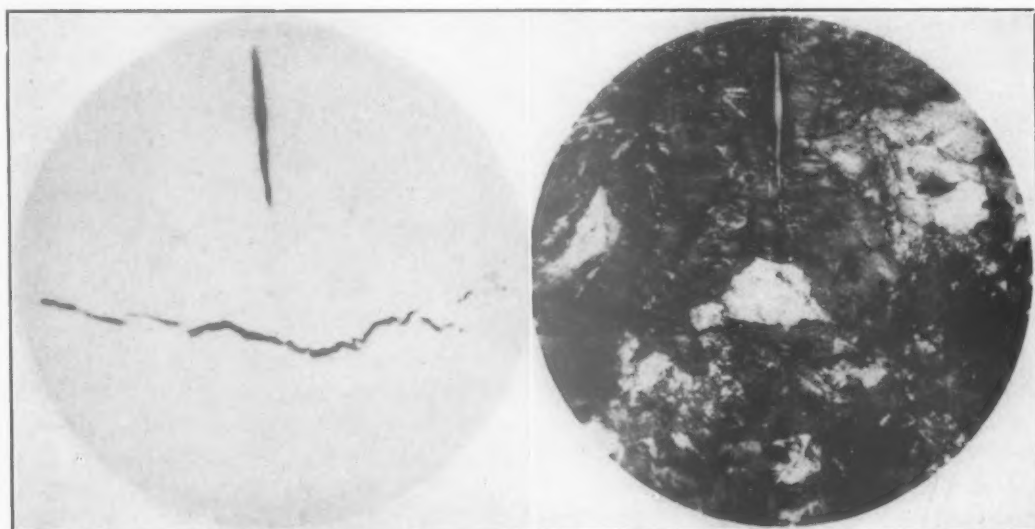


FIG. 19.—SPECIMEN *b* OF FIG. 18 SUBSEQUENTLY NORMALIZED AND BROKEN THROUGH TRANSVERSE CRACK.



Unetched

Etched

FIG. 20.—MICROSECTION OF SPECIMEN IN FIG. 19 SHOWING TYPICAL SLAG STRINGER NUCLEATING EMBRITTLED ZONE, AND TRANSCRYSTALLINE CRACK TRANSVERSE TO THAT ZONE. $\times 200$.

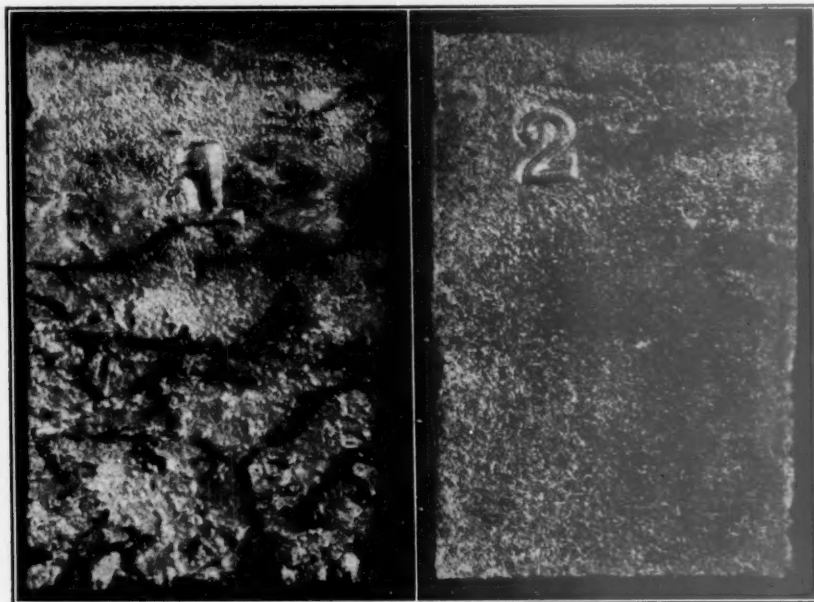
The stress operating there was due probably to differential transformation effects.

The specimen treated at 1200°C . was normalized to produce fibrous fracture (as in Fig. 17) in hydrogen-free portions of the

completely separated the rail, and the surrounding metal shows the hydrogen-embrittlement fracture. Only a skin layer is fibrous, indicating that the normalizing treatment removed but little hydrogen.

A microsection through this rail revealed slag stringers and fissures (Fig. 20). The flake in the photomicrograph appeared before etching. The localization of the flake

chemical reaction. On the other hand, cold deformation, it has been proved, opens internal spaces within steel, and Tammann and Bredemeier,⁷ as well as others,²² have



Hydrogen-embrittled

Normal

FIG. 21.—SPECIMENS FROM EDGES OF SHEETS IN FIG. 11 AFTER DEEP ETCHING IN HYDROCHLORIC ACID. $\times 3$.

about the slag nucleus, and its transverse direction and transcrystalline nature, nicely illustrate the argument that has been advanced.

SIGNIFICANCE OF HYDROGEN EMBRITTLEMENT IN CORROSION PHENOMENA

The concept of block structure and hydrogen embrittlement herein advanced carries some interesting implications regarding the corrosion of iron and steel.

It is well known that plastically deforming steel increases its vulnerability to chemical attack. Reasons given are vague but generally include the term "mechanical activation." It is not unreasonable to assume that the fragmentation attending plastic deformation at ordinary temperatures increases somewhat the fraction of atoms that are so badly out of position that they are especially susceptible to

shown by experiment that liquids penetrate metals and other crystalline substances in quantities that increase with increasing cold-work. The increased attack by chemical reagents that occurs with increasing cold-work then seems more likely to be caused by the increased surface for reaction that is provided by infiltration of the reagent through internal disjunctions.

If hydrogen opens the substructure network even more than does cold-work—as appears to be true, owing to the bloating effect of the gas on the disjunctions it occupies—hydrogen-embrittled metal should show a maximum susceptibility to chemical attack. That this is precisely what happens is shown by the following experiments.

Fig. 21 shows clippings taken from the edges of the two sheets in Fig. 11 after prolonged etching in 1:1 hydrochloric acid. The major fissures in the hydrogen-treated

specimen, it will be recalled, were developed during cold-rolling, but the entire sample reacted more violently with the acid and

is simply afforded by deep-etching the specimen shown in Figs. 6 and 12. This specimen (Fig. 23, right) shows conclu-

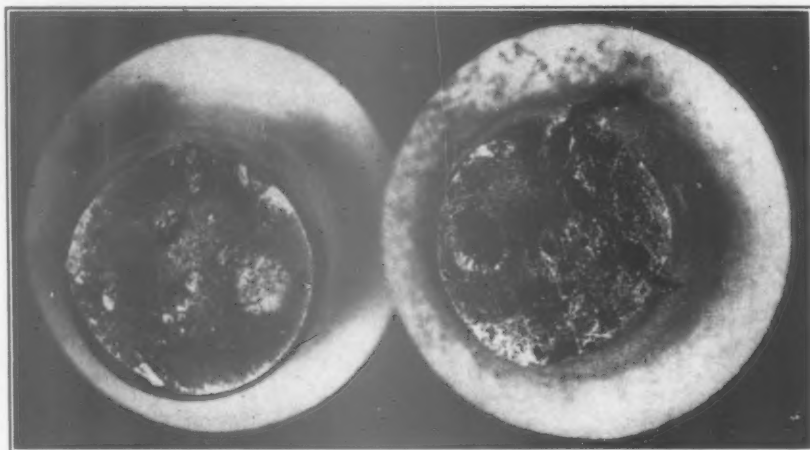


FIG. 22.—FRACTURE OF "FLAKY" TENSILE SPECIMEN SHOWING RESPONSE OF HYDROGEN-EMBRITTLED ZONES TO CHEMICAL ATTACK. $\times 2$.

is plainly more corroded than is the hydrogen-free sheet.

Fig. 22 shows a more striking example. One-half of a tensile specimen showing flakes was deep-etched in hydrochloric acid, and is shown in comparison with the other original fractured face. It is evident that each hydrogen-embrittled zone has dissolved with astonishing rapidity and completeness. Apparently the acid has infiltrated with great ease throughout the hydrogen-sprung disjunctions within the metal crystals themselves, permitting greatly accelerated dissolution. It is interesting here to recall that one investigator³¹ reported that solution of a crystal in a liquid occurs by ultramicroscopic blocks first being loosened by the liquid before dissolving. The hydrogen would aid such loosening.

The sideview of the other half of the specimen in Fig. 12 (left) is shown in Fig. 23 (left) after deep etching in hydrochloric acid. Here again the dissolution of the metal over the slag stringer was accomplished by the rift action of hydrogen and not by the presence of the slag, as supposed by some. Proof of this assumption

sively that the strongly preferential attack is due only to hydrogen, and that the attack proceeds through the rifts and fissures that have been opened by the gas.

In regard to Fig. 23, it is interesting to note that the specimen was not etched until nearly one year after its preparation. In that time the embrittling pressures of hydrogen were surely eliminated, so the reaction shown in the photograph represents a minimum effect. Furthermore, the specimen demonstrates that steel does not fully recover its physical properties after hydrogen is removed at ordinary temperatures, which is easy to understand when one abandons the hydride theory in favor of the block hypothesis. Such hysteresis should be expected if hydrogen acts analogously to cold-work.

EFFECT OF HEAT-TREATMENT ON DEFECTS CAUSED BY HYDROGEN

Fractional Nature of Hydrogen Liberation

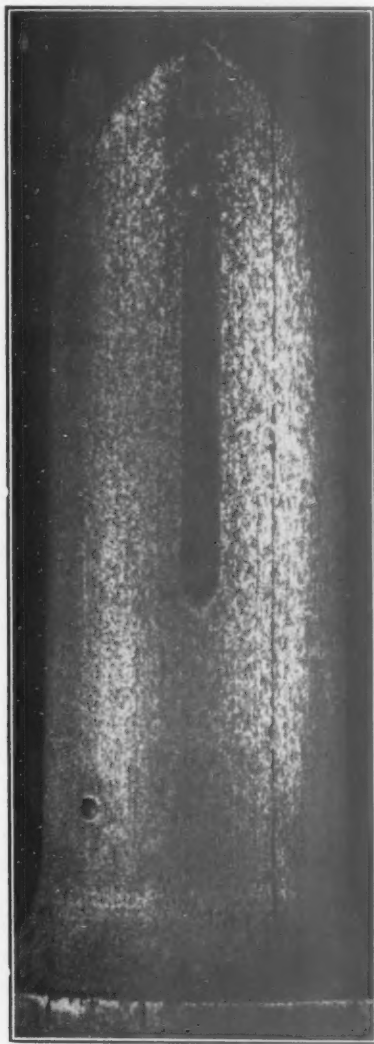
The many defects that have been discussed require the presence of hydrogen embrittlement for their formation, so it is

now important to find some method for preventing the occurrence of embrittlement and particularly to prevent the combined occurrence of embrittlement and critical internal stress. Prevention of hydrogen absorption during the making of steel is an obvious panacea but often is impracticable; and, because it has been carefully discussed elsewhere,^{104,108,110,111} it will not be reviewed here.

Each type of defect depends upon a certain aerostatic pressure of occluded gas for its formation. These pressures vary from several thousand atmospheres in connection



Ordinary



Artificial

FIG. 23.—TENSILE SPECIMENS FROM FIG. 12 DEEP-ETCHED IN HYDROCHLORIC ACID.

The alternative, removing the gas from the steel, generally involves heat-treatment and also has received much discussion. Some important considerations have been neglected, however, and the whole subject appears generally confused. The most serious misinterpretation is that the disappearance of certain hydrogen-caused defects connotes complete removal of the gas from the steel.

with embrittlement down to a fraction more than one atmosphere for blistering phenomena in paints and molten enamels. The pressure necessary for each particular defect should be referred to as the "critical pressure" for that defect; from which it follows immediately that a treatment removing embrittlement may still permit enough gas to remain to cause blister formation in sheet during subsequent

heating; disappearance of blistering in the sheet may still allow pinholes to develop from the remaining gas effusing during galvanizing or electroplating; and so on

removing hydrogen by low-temperature baking or aging so often fails in preventing subsequent formation of defects in electroplated, painted or enameled coatings.

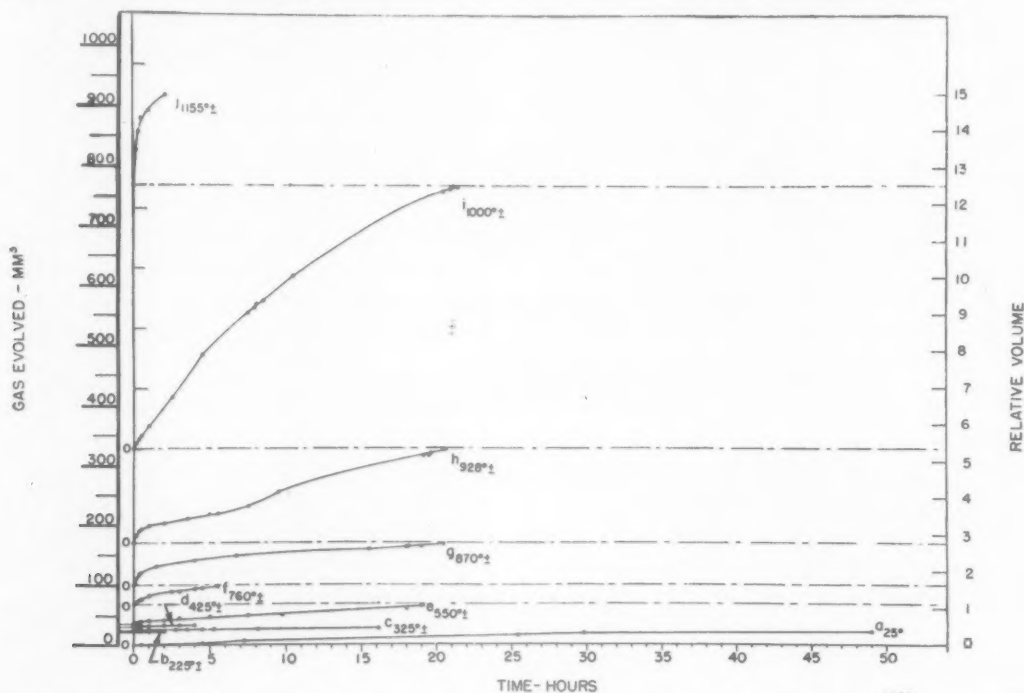


FIG. 24.—ISOTHERMAL EVOLUTION OF HYDROGEN FROM IRON FOIL, ACCORDING TO MOORE AND SMITH.

down through the chipping of vitreous enamel, finally to the blistering of soft paint and molten enamel. The point to be made is that only an increment, and sometimes a very small increment, of the absorbed hydrogen need be removed to preclude the development of the "critical pressure" necessary for some certain effect.

For the specific case of embrittlement, with which the present discussion is mainly concerned, it is necessary only to remove enough hydrogen so that at no point within the steel is there an aerostatic pressure exceeding the elastic strength of the material. That is why embrittlement is so easily eliminated at comparatively low temperatures, for a pressure reduction from 3000, say, to 2990 atmospheres can be accomplished with the diffusion that obtains at room temperature.* By way of corollary it should then be apparent why

Moore and Smith⁶⁹ have shown in a striking manner how hydrogen leaves the steel in "fractions" during annealing. They used thin iron foil so that occlusion in any loci other than block disjunctions would be quite improbable. Fig. 24 reproduces one of their important sets of curves and shows the step-wise liberation of hydrogen that occurs upon heating iron isothermally at progressively higher temperatures. Their explanation that internal rifts tend to heal upon heating, thereby driving occluded gas out of the steel, stands in full agreement with the present work and is corroborated in an interesting manner by other investigators⁴³ who believe that the healing together of blocks reaches end values for each progressive temperature increase.

A simple laboratory experiment to demonstrate the fractional nature of hydro-

gen removal entails loading a piece of steel with hydrogen and immersing it in transparent liquids heated to progressively higher temperatures. For each temperature the effusion begins rapidly and proceeds to an end point, only to repeat that same action when immersed at the next higher temperature. In Fig. 24, it may be seen that the effusion that occurs even at 225°C. is still but a fraction of the total gas contained in the iron.

*Explanation of Recurrence
of Hydrogen-caused Defects
after Heat-treatment*

One of the most puzzling anomalies in steelmaking has been the occasional recurrence of snowflakes, white spots and such defects after they have once been removed by heat-treatment. The explanation follows quite simply when distinction is made between the interblock occlusion of hydrogen that operates in simple embrittlement and the macro-occlusion that develops in the nucleus of the localized embrittlement identified as a flake or a white spot. In such localized defects a great quantity of hydrogen is stored in the nucleus because the relative size of that cavity is so great and the pressure there is a maximum.

When the maximum internal gas pressure has been reduced from 3000 to 2990 atmospheres, say, and is no longer sufficient to cause embrittlement, there may still be a greater quantity of gas stored in the nucleus than was formerly contained in the interblock rifts over the entire brittle zone of the flake. (See the volume curve in Fig. 10.) The fracture will be fibrous and will give every indication that the hydrogen has been removed. If reheated, however, as in normalizing, the steel comes to a temperature where the molecular gas in the nucleus can re-dissolve in the surrounding lattice, and the solubility can thereby be replenished beyond that necessary to raise the aerostatic pressure on cooling from 2990 back to 3000 atmos-

pheres. The fact that the recurring defect is always smaller and less extensively distributed than the original is in agreement with this reasoning, for some hydrogen is lost during each heat-treatment and the remaining gas therefore will support a smaller and smaller zone of embrittlement.

The conditions can easily be simulated in the laboratory by filling a hollow steel bar with hydrogen under pressure and sealing it. Obviously the bar is not embrittled, for steel tanks are used commercially for storing hydrogen and never become brittle. However, if the bar is heated, as in normalizing, the gas will dissolve into the steel and upon cooling the metal will be embrittled throughout. A cross section of the bar then resembles a fisheye,¹⁰⁶ but the pressure within the bore in this case is plainly even less than it was originally, although the pressure within the rifts of the surrounding metal exceeds the yield strength. The embrittlement in such a specimen will be relieved by precipitation of the gas both inside and outside the bar, and concentric rings of ductile metal will develop at both surfaces. In naturally occurring fisheyes, the ductility advances only from the outside toward the center.

*Response of Hydrogen Embrittlement
to Annealing*

A group of tests was run to determine the most efficient annealing temperature for removing hydrogen embrittlement and to find in general the behavior of hydrogen in steel over a temperature range. Theoretically, annealing would be most efficient at some elevated temperature that lies below the "critical temperature for embrittlement," which is the temperature above which the solubility decrease on cooling would cause hyperelastic aerostatic stress to develop. There the ratio of the diffusibility, which increases logarithmically with increasing temperature, to the solubility of hydrogen in steel would be a maximum, and removal of the gas would

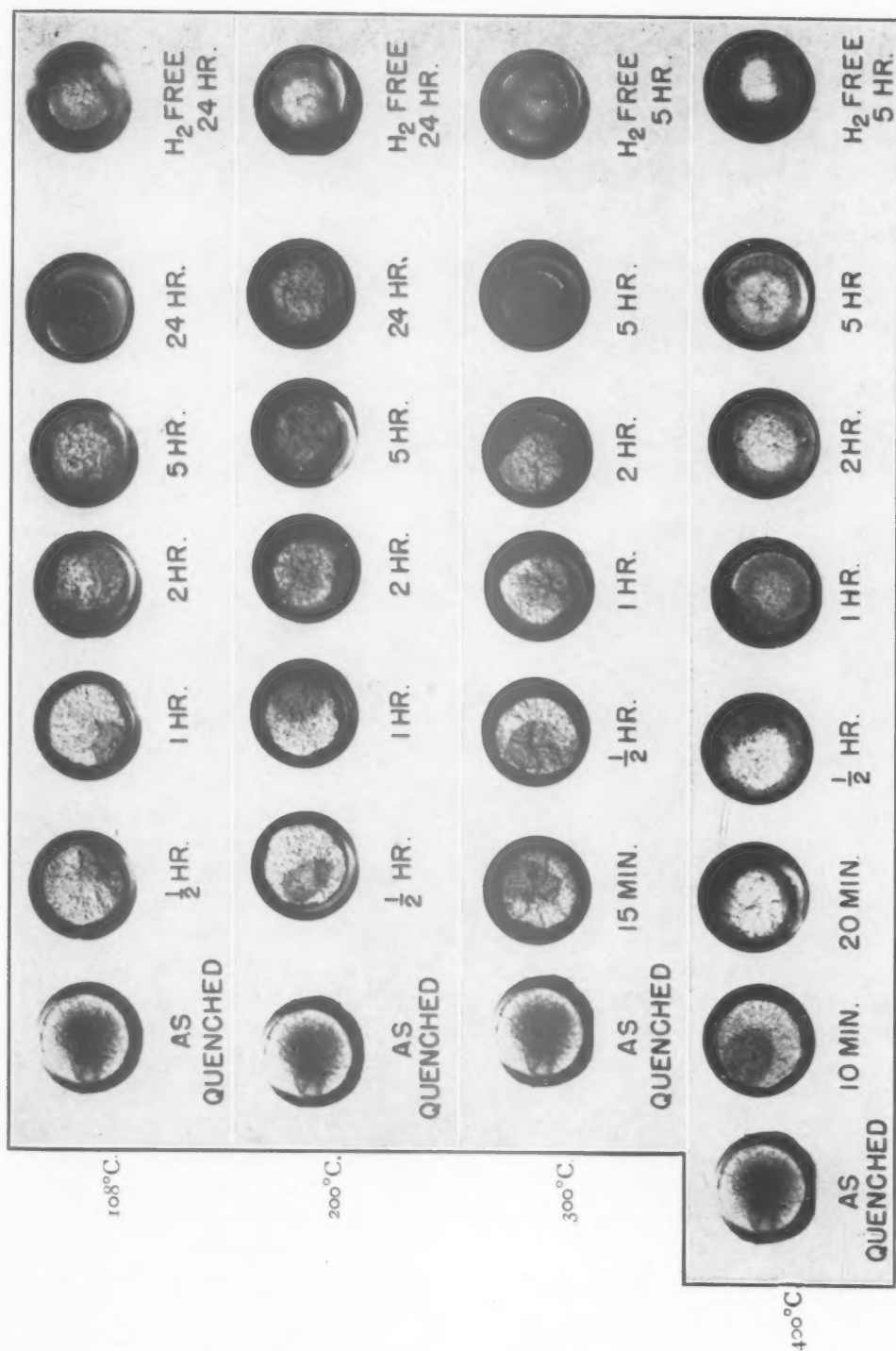


FIG. 25.—TENSILE FRACTURES OF MILD STEEL ANNEALED IN HYDROGEN FOR THREE HOURS AT 1100°C., QUENCHED AND SUBSEQUENTLY ANNEALED AS INDICATED.

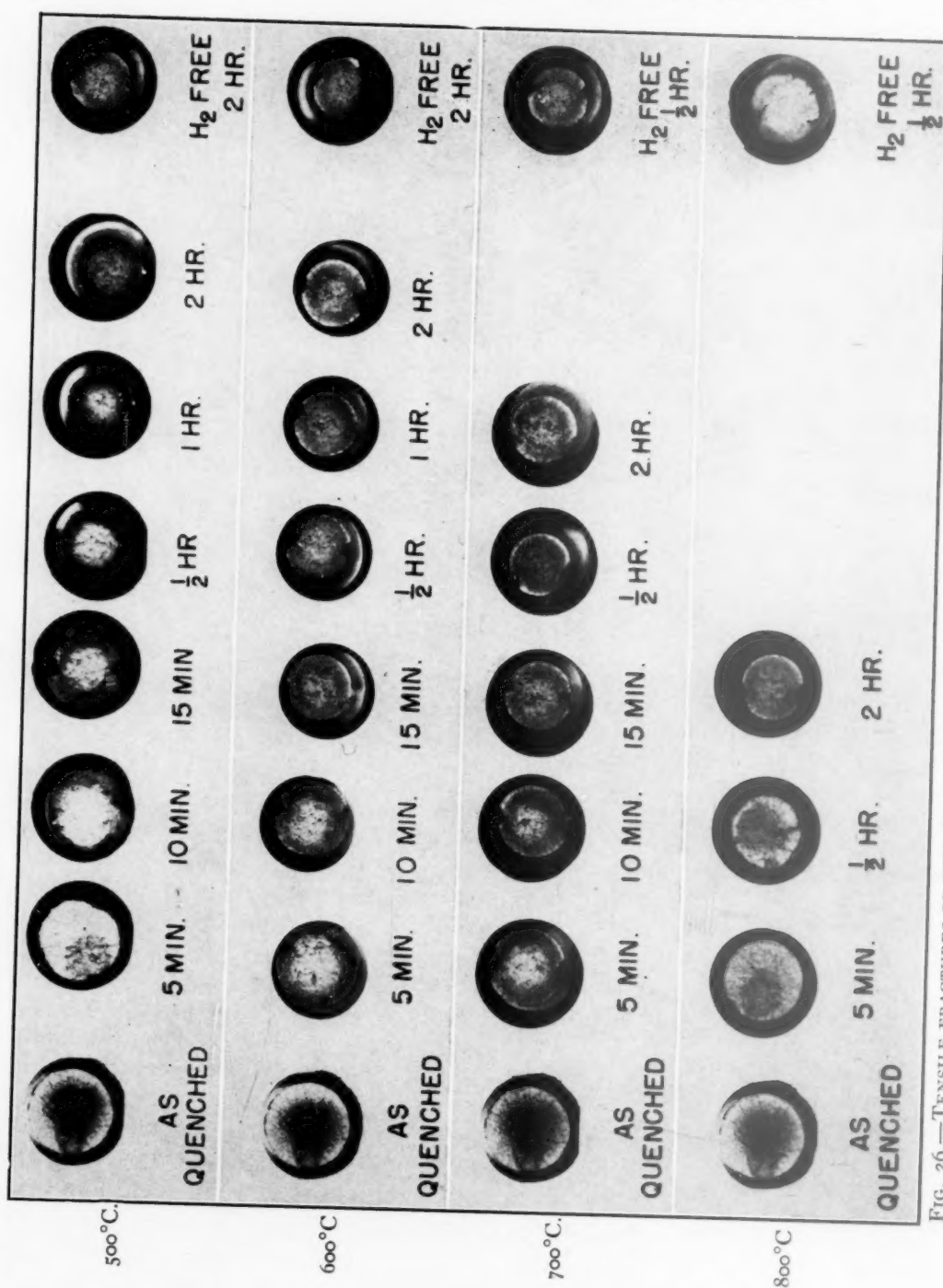


FIG. 26.—TENSILE FRACTURES OF MILD STEEL ANNEALED IN HYDROGEN FOR THREE HOURS AT 1100°C., QUENCHED AND SUBSEQUENTLY ANNEALED AS INDICATED.
(Continuation of Fig. 25.)

therefore be most efficient. The atmosphere, of course, has such an important relation that no such single temperature exists. In general, though, the increase in solubility at the transformation temperature is so marked that one would expect most rapid annealing effects to occur just below 725°C .

A group of 0.505-in. mild (0.18 carbon) steel tensile specimens was heated in hydrogen for 3 hr. at 1100°C . and was quenched in water to afford maximum retention of hydrogen. These specimens were then treated for varying periods of time at temperatures from 100° to 800°C . in 100° intervals. At the termination of the treatment each specimen was again quenched so that hydrogen loss on cooling would not modify the results. The specimens were immediately tested in tension and the resulting fractures are shown in Figs. 25 and 26.

Another set of bars containing no hydrogen was quenched from the same heat-treatment in the absence of hydrogen and subsequently was annealed for use as control specimens. The annealing periods were the same as those of the particular specimens with which they were later to be compared, and the effects of microstructural changes from quenching were thereby eliminated from the comparison.

The fractures of these tests are significant. The disappearance of the shiny embrittled zone with increasing time is easy to follow, and the close resemblance of hydrogen-free and hydrogen-removed specimens after critical annealing periods can be taken as an indication that the deleterious effects of the gas are gone as far as embrittlement is concerned.

Of especial importance is that the embrittlement disappears with increasing rapidity as the temperature is raised, being most rapid at 700°C ., but that at 800°C . $\frac{1}{2}$ hr. hardly changes the embrittled condition, 2 hr. being required to bring good ductility. (Note the retention of the brittle

zone in Fig. 26.) That result conforms with the expected effect from re-solution of hydrogen above the transformation temperature, as just explained.

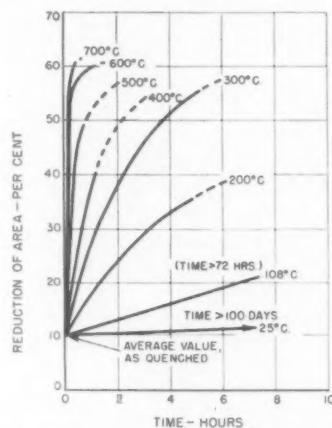


FIG. 27.—DUCTILITY CHANGES IN FOREGOING SPECIMENS.

The ductility of these specimens as measured by the percentage reduction of area showed the relationships with temperature and period of anneal as sketched in Fig. 27. Strength values were also measured but will not be reported, for they have no significance. Hydrogen embrittlement in itself has no particular effect on the ultimate strength of steel.

From an examination of these specimens, the time interval of annealing was chosen at which "near maximum" ductility was first obtained (point of rapidly changing curvature in Fig. 27), and the control specimens were then annealed for that particular length of time so that conditions of precipitation and recrystallization would be identical in corresponding groups and only the hydrogen contents would differ. Ductilities of the hydrogen-free group were assumed to represent end-point ductilities for the hydrogen-removed specimens, and the curve shown in Fig. 28 was constructed to show the variation with temperature of the length of anneal necessary for obtaining relief from hydrogen embrittlement—that is, for obtaining "near maximum" ductility. The shape of the

curve conforms with theoretical expectations and shows that relief becomes more rapid as the transformation temperature is approached, but that complete relief

brittling quantities of hydrogen as 100 days at 25°C.

Important to note is that good ductility ultimately can be attained by annealing

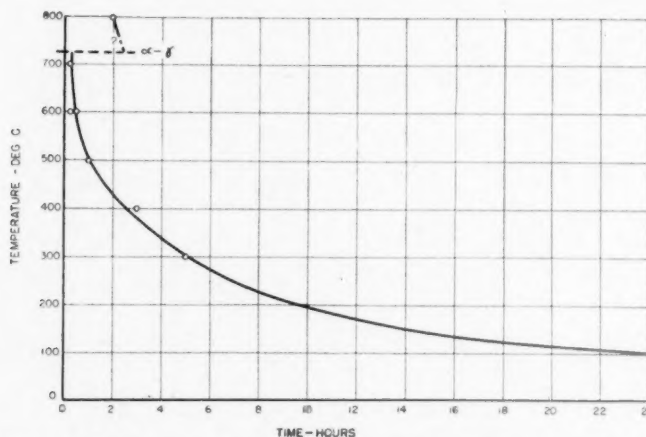


FIG. 28.—RELATION OF TEMPERATURE TO ANNEALING TIME NECESSARY FOR REMOVING HYDROGEN EMBRITTLEMENT FROM FOREGOING SPECIMENS.

(from embrittlement) is also possible at lower temperatures with extended annealing periods. Needless to say, the values are only approximate and at best are quantitative only for the specimens under consideration. Size of section and composition of the steel strongly affect these values.

Representation in Fig. 28 of the behavior above the transformation temperature is diagrammatic and has for its basis that the solubility disjunction probably causes a similar disjunction in this particular curve; and each section of the displaced curve probably shows the same type of curvature because the diffusibility remains a temperature function. Moore's curves in Fig. 24, which steepen progressively from room temperature to 1155°C., seem to substantiate the present selection. Finally, the point at 800°C. was determined experimentally, so the curve between 700° and 800° must be either displaced or reversed.

In Fig. 27 a line has been inserted for ductility change at room temperature. The data were obtained from the specimens shown in Fig. 3 and conform well with known facts by showing that one day at 108°C. is as effective in removing em-

at these low temperatures. The fact is important in fabrication of products that do not permit annealing at higher temperatures. Another important aspect is that steel produced and treated in ordinary manners likewise shows some increase in ductility during annealing at low temperatures, and that that ductility increase is due to little-suspected hydrogen removal.

Behavior of Hydrogen in Weld Metal

The foregoing specimens, it should be remembered, in general lacked macroscopic internal inhomogeneities and their behavior therefore represents that of simple hydrogen embrittlement. In weld metal numerous inhomogeneities occur and the prevalence of localized "fisheye" defects makes it interesting material with which to work. From earlier discussions it can be realized that the large quantities of gas contained in the nuclei of fisheyes may introduce a factor that complicates the reactions just discussed for plain steel.

Weld metal is most amenable to hydrogen-caused defects because the atmosphere and the superheating in most welding is conducive to hydrogen absorption. The

defects in arc-welded steel have been discussed in another publication,¹⁰⁶ so discussion here will be limited to a few essential observations.

Figs. 7, 8 and 9 have already shown hydrogen-caused defects of the type found in weld fractures. The importance of the

The variation of the ductility is in agreement with the work on plain steel; the behavior of the tensile strength is anomalous but may be concerned in some way with the precipitation of oxides.

Plainly, the atmospheric humidity largely controls the moisture content of the elec-

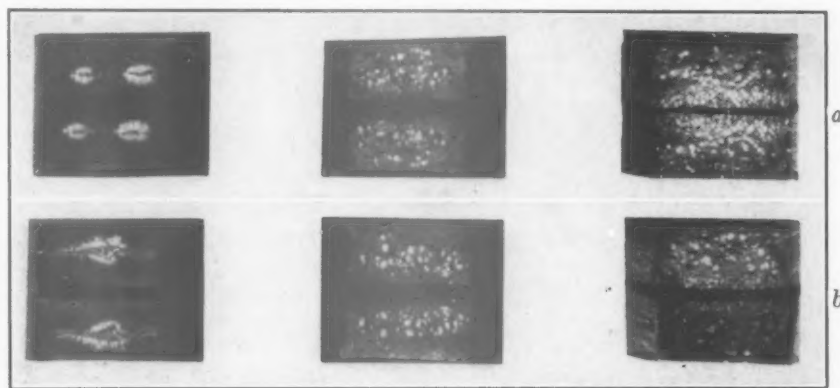


FIG. 29.—TENSILE FRACTURES OF ARC-WELDED SPECIMENS SHOWING EFFECT OF MOISTURE IN THE ELECTRODE COATING.

presence of moisture in causing these defects and in determining their appearance is shown in Fig. 29. Welds made with cellulose-coated electrodes previously dried at 108°C. showed only a collapsed brittle zone at the inter-bead disjunction, whereas ordinary electrodes used in ordinary atmospheres or under steam showed very mottled fractures with wide dissemination of the defects. The moisture apparently reacts with the metal during welding to form trapped oxides and at the same time liberates nascent hydrogen in quantities that greatly aggravate the total absorption. The dissolved hydrogen precipitates in and around the resulting included solid oxides and also reacts with dissolved oxygen to form steam that forms blowholes. Each of the discontinuities gathers the gas during cooling to give the mottled embrittlement shown on the fractures in Fig. 29.

This effect of moisture contained in the electrode coating is sketched in Fig. 30.*

* The physical properties from which this graph was constructed may be found in reference 106.

trode. Fig. 31 shows how strongly humidity determines the appearance and abundance of hydrogen-caused defects in the weld

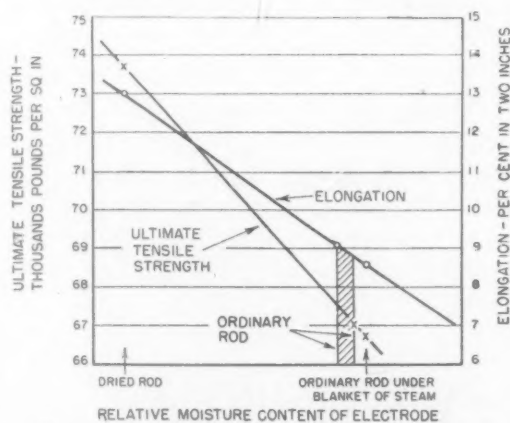


FIG. 30.—EFFECT OF MOISTURE IN ELECTRODE COATING ON PHYSICAL PROPERTIES OF THE WELD. (RELATIVE HUMIDITY 36.)

fractures, and Fig. 32 shows the response of the physical properties. Fractures of welds made in humid weather show the mottled type of embrittlement, whereas in dry weather the defects are much less numerous and less localized.

To illustrate how the localized type of embrittlement responds to annealing, a series of arc-welded specimens was treated

but contained only ordinary quantities of the gas. The fractures of the 106°, 700° and 800°C. groups are shown in Fig. 33.*

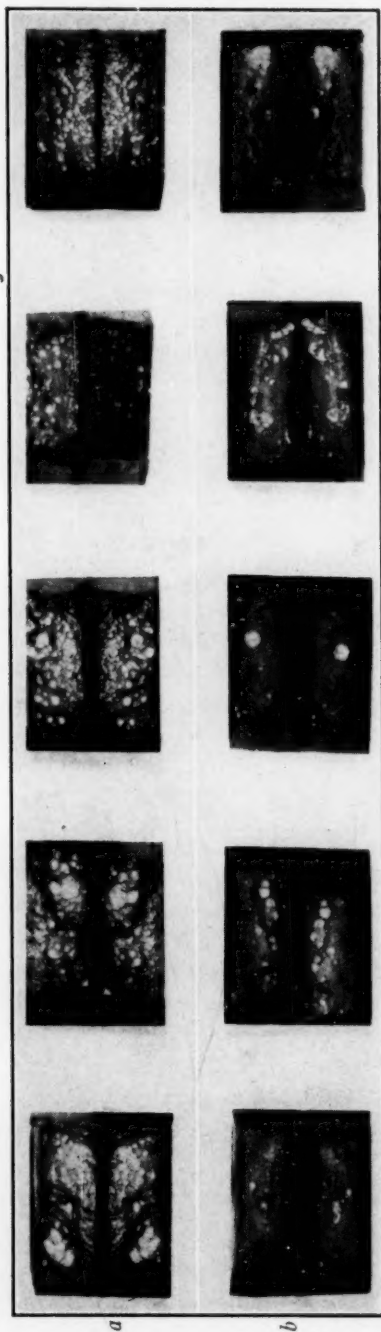


FIG. 31.—TENSILE FRACTURES OF ARC-WELDED SPECIMENS SHOWING EFFECT OF ATMOSPHERIC HUMIDITY.
a, welds made in humid weather; b, welds made in dry weather.

identically as were the previous mild-steel specimens. The weld specimens, however, were not artificially loaded with hydrogen,

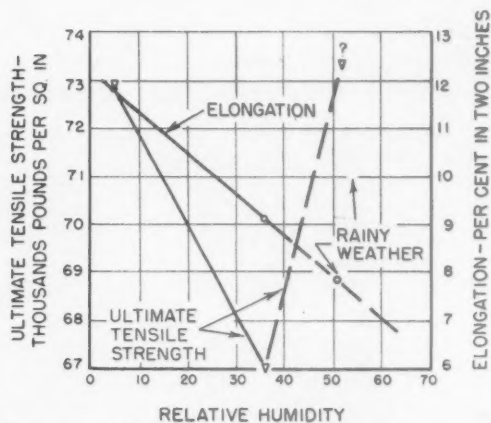


FIG. 32.—EFFECT OF ATMOSPHERIC HUMIDITY ON PHYSICAL PROPERTIES OF WELD.

The effects of the heat-treatment were generally the same as for the corresponding tests with plain carbon steel except for two interesting differences. First, the period of time necessary for removing the embrittlement at low temperatures was greater for the weld metal and depended upon the amount of macro-occlusion; that is, a fisheye is eliminated more slowly than is the same area of simple embrittlement because more gas is concerned. Nevertheless, remarkable ductility may result from aging at 106°C., as is shown in the figure. Second, whereas 700°C. was a most effective annealing temperature for removing embrittlement from plain carbon steel, weld specimens at the same temperature remained embrittled throughout. (Compare the fractures in Fig. 33.) The retention of embrittling quantities of gas at 700°C. in weld specimens follows directly from the reasoning just used in explaining the recurrence of flakes. The texture of the weld metal is relatively porous and large quantities of gas under high pressure are concerned. Even after 2 hr. at

* For a more careful discussion, see reference 106.

700°, and also at 800°C., embrittled zones were still visible, although heating a few minutes at 600°C. was sufficient to remove them. The pores in the weld metal have

2. In the network of disjunctions that give these blocks their identity, hydrogen occludes, perhaps as partially ionized molecules. The occlusion is associated with

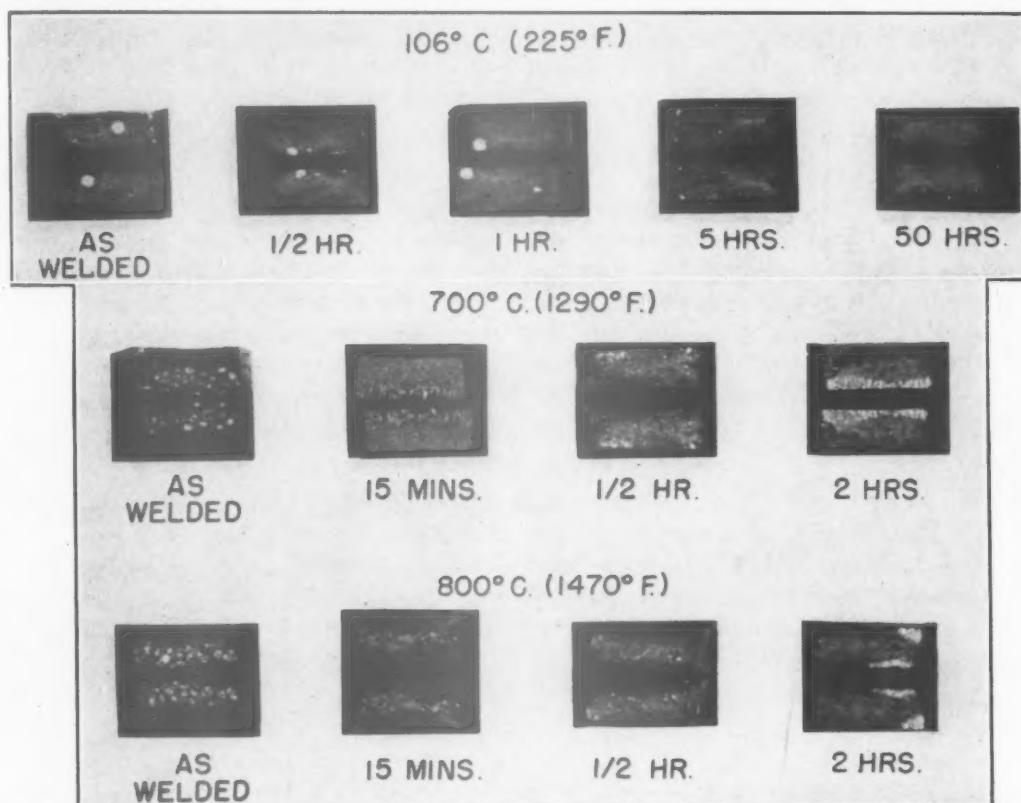


FIG. 33.—TENSILE FRACTURES OF WELD SPECIMENS SHOWING EFFECT OF ANNEALING ON DEFECTS CAUSED BY HYDROGEN.

acted as reservoirs of hydrogen, and even the limited solubility of α iron has permitted sufficient re-solution in its upper temperature range to cause retention of embrittling quantities of the gas.

CONCLUSIONS

From the foregoing it seems necessary to conclude that:

1. Steel, like other crystalline substances, probably is constructed of some unidentified type of multi-atom unit which can be referred to as a block. Such a unit is roughly of the order of 1000 atoms on an edge, lying at the lower limit of resolution of the microscope, and from it are built the visible crystals.

the development of pressure and, when this pressure exceeds the elastic strength of the steel, the disjunctions are "sprung," forming cleavage and slip elements, much as in cold-work.

3. Hydrogen embrittlement is the phenomenon just named, and the bright fracture that characterizes this defect can be explained as being due to the favorably oriented flat reflecting facets of the groups of blocks across which the break has proceeded.

4. The opening of the block disjunctions by the high pressures of occluded hydrogen permits liquids to penetrate crystals of steel that have been embrittled

by hydrogen, and subsequent chemical attack is greatly enhanced by the infiltration.

5. The embrittlement conferred by hydrogen is well explained by the block concept, for the pressure of the occluded gas is aerostatic and therefore is exerted triaxially. Metal stressed triaxially cannot flow, and only rupture can relieve a superimposed stress.

6. "Snowflakes," "fisheyes," "white spots," "birdeyes," "snake-eyes," "rosettes" and "silver streaks," to name but a few, are merely hydrogen embrittlement that has localized around some interstice, inclusion or blowhole.

7. "Checks" or "tears" on the surface of tensile specimens can be caused by hydrogen embrittlement near the surface, which precludes flow of that region during tensile testing.

8. "Flakes" and "shatter cracks" are internal hydrogen-embrittled zones that have cracked from superimposed internal stresses, among which cooling stresses are the most important. Rim-core shrinkage is often a very important source of internal stress; and the slag stringers are the important loci for nucleation of the embrittled regions. Flakes therefore are most often oriented in the rolling or forging direction perpendicular to that stress. Longitudinal shrinkage accounts for transverse flaking, which is generally much less abundant than the other. Transformation stresses are an important factor, because the sharp volume change occurring when austenite transforms aggravates internal stresses. An alloying element such as carbon is often crucial, therefore, for the development of flakes because the stresses developing during transformation are a maximum, and on rapid cooling they may occur at temperatures where they cannot be relieved. Also, the solubility of hydrogen in steel decreases sharply at the transformation temperature, which favors development of the high aerostatic pressures necessary to cause embrittlement.

9. Embrittling quantities of hydrogen are most rapidly removed from plain carbon steel at a temperature just below the transformation temperature. Above this temperature the gas may largely remain in the steel because the solubility increases so markedly.

10. If the steel contains hydrogen in cavities that are not the block disjunctions in question, such as in weld metal, that hydrogen may re-dissolve in injurious quantities at temperatures somewhat below the transformation temperature. Also, longer times are then necessary for removing embrittlement because larger quantities of gas are involved.

11. Re-solution of hydrogen from seats of macro-occlusion accounts for the occasional recurrence after normalizing of hydrogen-caused defects such as flakes and white spots.

SUMMARY

The concept of "block" structure in steel is discussed and the proposal is made that hydrogen embrittlement is the phenomenon of occlusion of hydrogen under high pressure in "interblock disjunctions." These disjunctions appear to be a fundamental part of crystal structure and are related to slip and cleavage phenomena. When the occlusion pressure exceeds the elastic strength of the steel, the disjunctions are sprung and slip and cleavage planes operate much as during cold deformation. The bright fracture that always characterizes the transcrystalline type of hydrogen embrittlement is consequently explained as being due to reflection from flat cleavage facets that separated along planes favorably oriented with the imposed stress. Opening of this ultramicroscopic structure of steel by hydrogen can be illustrated experimentally, for liquids readily penetrate hydrogen-embrittled steel.

Hydrogen embrittlement, if caused by aerostatic pressures within the substructure

ture, or the cleavage structure, of steel, must have the nature of triaxial stress and will therefore inhibit flow, so that an imposed stress may lead to rupture. "Snow flakes," "white spots," "fisheyes," "silver streaks" and such defects that do not necessarily exhibit fissuring are shown to be hydrogen embrittlement that is localized about some discontinuity, such as an interdendritic interstice, inclusion or blowhole. "Flakes" and "shatter cracks," which are fissures, are shown to be similar hydrogen-embrittled zones that are subsequently ruptured by imposed stress. "Checks" or "tears" on the surface of tensile specimens may be caused by hydrogen embrittlement just as are "flakes," except that the imposed stress causing "tears" is specifically from tensile testing. The mechanism of these defects and their interrelationships are discussed and illustrated by experiment.

Recovery from hydrogen embrittlement upon annealing is investigated both for mild steel and for weld metal. Optimum annealing treatments for improving ductility are suggested, and re-solution of hydrogen from rift-to-lattice at elevated temperatures is demonstrated to explain the puzzling recurrence of hydrogen-caused defects in steel from which hydrogen had apparently been removed.

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DISCUSSION

(Frank T. Sisco presiding)

H. STYRI,* Philadelphia, Pa.—The authors have given plenty of evidence that hydrogen has strong embrittling effect in steel, and thereby verified common knowledge. One gets the impression from a study of the paper, however, that hydrogen is the principal bad actor in making steel brittle and that if it were not present in sufficient quantities, such things as flakes or snowflakes could not occur.

To many investigators who studied "flakes" during the "epidemic" of the last war, this hydrogen bugaboo does not seem adequate to explain all the troubles. In the writer's own experience, it was not possible to eliminate flakes from gun forgings by any kind of heat-treatment, if they were once found in a forging. The physical properties would, of course, be affected and there would be a variation in quantity of flakes found in different samples taken from the same forging. Most of these flakes probably were not actual cracks but weak spots. In the early 1920's the writer again met the problem of flakes, this time in ball-bearing steel, particularly in hot-rolled bars. Extensive heat-treatment experiments were performed in an effort to eliminate the flakes, but without success. It was found that in this case the flakes were actual cracks, which, however, were not visible to the naked eye but could easily be located in the section by magnetic testing, by etching, or simply by bending. After intensive investigation it was shown that the flakes could be eliminated by slight forging followed by slow cooling. Flakes in ball-bearing

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steel were thoroughly discussed by Hultgren in 1925.¹¹³

In view of the results reported in the present paper, one must assume that in many experiments most of the hydrogen would have been expelled during repeated long-time heatings, and that, therefore, according to Zapffe and Sims, the steel should not show brittleness. It would, for instance, be difficult to believe that a sufficient amount of hydrogen could remain in a ring forging 1½ in. thick, 4 in. wide and 16 in. in diameter to cause formation of snowflakes in the section, after this ring had been forged from a slug that was cut from an annealed billet by cold sawing and heated to forging temperature, then pierced and forged on a mandril, cooled and annealed for machining. From our experience, the flakes evidently were formed during cooling after forging.

On the other hand, it is now common knowledge that flakes can be avoided, in manufacturing, by slow cooling after hot-working, as first reported by Hultgren. Stresses due to temperature difference between outside and core by rapid cooling from a sufficiently high temperature seem necessary to produce flakes in hot-rolled bars. With sufficiently slow cooling, at least through a certain temperature range down to 200°C., flakes do not occur.

A large number of slag inclusions that were found so prominent in flakes in gun forgings in the 1917-18 period, probably greatly affected the ductility of the steel.¹¹⁴ The snowflakes found in bearing steel, however, were not thus contaminated.

We have had some experience that may throw additional light on the causes of brittleness. In a steel containing 0.50 per cent C and 2 per cent W, we occasionally found excessive brittleness that could not be eliminated by any heat-treatment, but only by reforging. Extensive investigation proved that the brittleness was associated with too coarse austenite grains. The fractures were much like fractures with fish scale in high-speed steel reported by Brophy (Amer. Soc. Steel Treat., 1932) and by Gill (Amer. Soc. Steel Treat., 1936). It seems probable that the experience reported by Foley—namely, that flakes were found in the end of the ingot that was heated to temperature of 1400°C. but not in the end heated to 1200°C.

—may be due to the coarser structure of the hot end. The author's results in experiments on 131-lb. rails may be explained also by greater brittleness with a coarser grain developed by heating in hydrogen to the higher temperature of 1200°C., compared with heating to 1100°C., and controls should have been run on rails heated under ordinary furnace atmosphere.

It is well known that internal bursts and porosities can be produced by improper forging practice, and it is also known that by proper forging practice flakes may be avoided, as shown, for instance, in Wahlsteen's American Patent No. 1966602.

It therefore seems unreasonable to blame hydrogen for all or most of the trouble with brittleness that occurs in processing certain steels. It seems instead that other causes may be completely responsible, even in the absence of hydrogen (admittedly difficult to prove); namely, hot-working with finishing at too high a temperature, so that coarse austenite grains remain, rapid cooling in certain temperature intervals setting up cooling stresses due to temperature differences between core and surface, presence of imperfections such as slag or blowholes or segregation in the steel.

F. B. FOLEY,* Nicetown, Philadelphia, Pa. The authors of this paper make out an excellent case for hydrogen as the agent responsible for "flakes" and kindred defects in steel and support it with interesting hypotheses. One of the obstacles to agreeing wholly with the hydrogen hypothesis is that almost all the evidence for it is based on the introduction of large quantities of the gas into the metal, amounts that seem to be so far in excess of what would ordinarily be expected to find their way into steel under normal conditions of melting. When steel that has developed cooling cracks is analyzed for hydrogen, the amount reported is rather small, but then it may be argued that much of the hydrogen ordinarily present has been driven off during heating for forging and for the production of the desired physical properties. Undoubtedly hydrogen can produce the types of defects known as "cooling cracks," "flakes," "fisheyes," "transverse fissures," but it has not been shown conclusively that hydrogen by itself is the only agency responsible for their occurrence. While repeated heat-treat-

¹¹³ *Jnl. Iron and Steel Inst.* (1925).

¹¹⁴ *Chem. and Met. Eng.* (April 1919).

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ments have been known to reduce the size of one type of "flake" in ordnance steel, it has not been shown to effect the complete removal of them. For example, repeated heatings of a "flaky" gun forging successively to 1600°F. (871°C.), 1500°F. (816°C.) and 1400°F. (760°C.) with holding times of 2 hr. followed by drawing 2 hr. at 1200°F. (649°C.) increased the average elongation from 3.75 to 11.5 per cent and apparently reduced the percentage of "flake" area from 64.1 to 9.7 per cent. The authors have shown complete restoration of the fracture appearance and of the ductility of hydrogenized metal by single heatings for shorter time periods. Reclamation by heat-treatment of welds in which "fisheyes" appeared was more difficult, although the "fisheyes" were not produced by artificial hydrogenizing. This difference in response to heat-treatment is attributed to greater content of hydrogen in the welded specimens and to its escape into voids from which it is assumed to have been reabsorbed. It is doubtful whether this explanation accounts for the reluctance of nickel ordnance steel to undergo reclamation by heat-treatment.

When cooling cracks were found in nickel ordnance steels following forging, and before any heat-treatment was applied, they were found to be associated with an extremely large austenitic grain size and they followed grain boundaries. It would be interesting to learn whether hydrogen promotes austenitic grain growth. The presence of the cracks in grain boundaries indicated that they occurred while the metal was in the austenitic form, unless it be assumed that rupture sought the weaker ferrite after the transformation had become complete. In recent years it has been shown by Bain that austenitic grain size influences the temperature at which transformation starts during cooling; large grains tending to lower it. This shifting of the transformation to lower temperatures may well have a bearing on the tendency to formation of cooling cracks, by causing the transformation to occur in a critical range. Of course, the grain size of austenite is a function of the temperature of forging, but it is well known that the presence of certain elements has an effect on the temperature and rate at which grain growth proceeds. The effect of hydrogen in this direction and aside from

its direct physical effect in creating pressure might bear looking into.

R. E. CRAMER,* Urbana, Ill.—The members of the Test Party of the Rails Investigation at the University of Illinois have enjoyed all of Messrs. Zapffe and Sims' papers on hydrogen in steel, and we especially like this one, which deals with subjects with which we are interested in connection with the investigation of fissures and shatter cracks in railroad rails. It is satisfying to find that the authors' results and opinions are in good agreement with our observations on hydrogen in rail steel and some defects it can cause.

Our work has been confined to railroad rail steel and has included some work on welded rails. For that reason we are particularly interested in the authors' work on "behavior of hydrogen in weld metal" and their discussion of "fisheyes," "white spots" and "silver streaks." The authors have not stated whether or not they considered that these defects existed before the specimens were pulled in the tensile tests. From our work on shatter cracks in rails, we would suspect that all three defects—that is, "fisheyes," "white spots" and "silver streaks"—might at least in some cases be present in the specimens as internal cracks before they were tested. On a fracture they all appear bright in contrast to the surrounding silky grains, probably because there is no deformation of the grains along the faces of the crack while the surrounding grains are plastically deformed during the necking down of the specimens, which gives them a gray, silky appearance.

Recently I had an opportunity to observe the fractures of some welded tensile specimens tested in our laboratory, which I think confirms this opinion that at least one such defect existed as a crack before the specimens were fractured. The welded specimens were plates about $\frac{7}{8}$ in. thick and had been machined to 5 in. wide at the critical section. They were brought into the laboratory in wooden crates on a cold day. Considerable moisture collected on the cold steel, which formed a light rust on the bright machined edges of the specimens and would have penetrated into any cracks that extended to the edges of the specimens.

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Fig. 34 shows the fracture of one of these specimens at natural size, which has a "silver streak" in the center of the weld the full width of the specimen besides some "fisheyes" and coarse crystals along one edge. At the edge of

R. S. ARCHER,* Chicago, Ill.—The authors have brought together in a very interesting way a great deal of scattered evidence pointing to the probable role of hydrogen as a cause of certain defects in steel. An explanation is thus

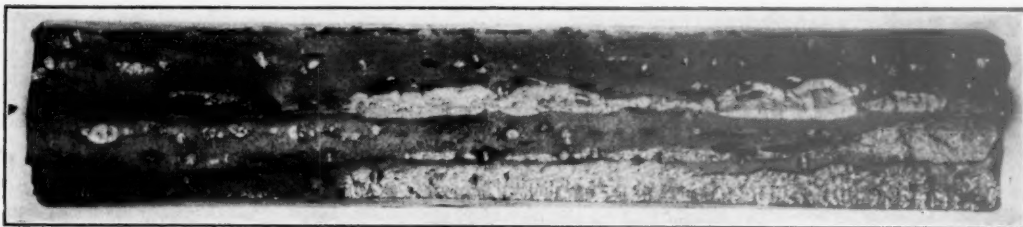


FIG. 34.—FRACTURE OF WELDED TENSILE SPECIMEN.

the specimen marked with an arrow the silver streak is oxidized and appears black. This was also true of the opposite face of the fracture. From this observation, I conclude that this area was cracked and had corroded before the specimen was tested.

I would, therefore, like to ask the authors if they have information as to whether such defects existed as cracks before their specimens were fractured?

S. EPSTEIN,* Bethlehem, Pa.—This review of hydrogen embrittlement in steel and the suggestion that such embrittlement may be connected with the "block" structure of steel, is most interesting. A point that impressed the writer is the statement that hydrogen absorption, like cold-working, tends to remove the yield-point phenomenon. Presumably this means that the nick in the stress-strain curve at the yield point, which is present in low-carbon annealed steel, is absent when hydrogen has been absorbed by the steel. In view of the widespread interest in the yield-point phenomenon, it would seem desirable to illustrate the effect of hydrogen upon it, by actual stress-strain curves before and after hydrogen absorption and possibly after aging. The cause of the nick in the stress-strain curve at the yield point is rather obscure and the observation the authors have mentioned may throw some light on the problem. It might also be of interest to determine whether hydrogen has any effect on blue-brittleness—that is, does it tend to increase or lessen the difference in tensile strength between samples tested at 400°F. and at room temperature?

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offered for many phenomena which have been puzzling. For example, a recent article in a trade paper describes the improvement in the ductility of steel deposited by gas welding, which results from aging or annealing at very low temperatures. This article does not, however, offer any explanation of the improvement.

The authors' description of experiments on 0.18 carbon steel specimens described on page 253 is not clear. It also seems that the changes in ductility and in the fractures represent the combined effect of tempering a quenched steel and the assumed effect of removal of hydrogen. It is possible that the authors intended these experiments only as a qualitative illustration of their thesis rather than as a proof. There is a need for more exact proof of the various effects attributed to hydrogen. The whole story seems plausible and even probable. Any positive control of hydrogen in liquid or solid steel promises to be difficult. It is, therefore, important that the effects of hydrogen be very thoroughly established.

The authors seem to have adopted the conception of a block or mosaic substructure in metals and also seem to feel that the observations recorded in their paper indicate such a structure. Actually it may be said that their observations are consistent with such a structure but do not indicate or verify it. It is possible that some of the observed facts may be due to periodic distribution of impurities rather than to an inherent characteristic of pure crystals. This point, of course, is not vital in the general picture of hydrogen embrittlement which the authors have presented so well.

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N. P. Goss,* Youngstown, Ohio.—This paper by Zapffe and Sims will without question become a classic when the significance of its contents is more widely accepted and appreciated.

edge concerning its nature and physical characteristics. To explain certain phenomena of the solid state, such as the plastic flow of metals under external forces, the physicists have been compelled to assume the existence of some sort

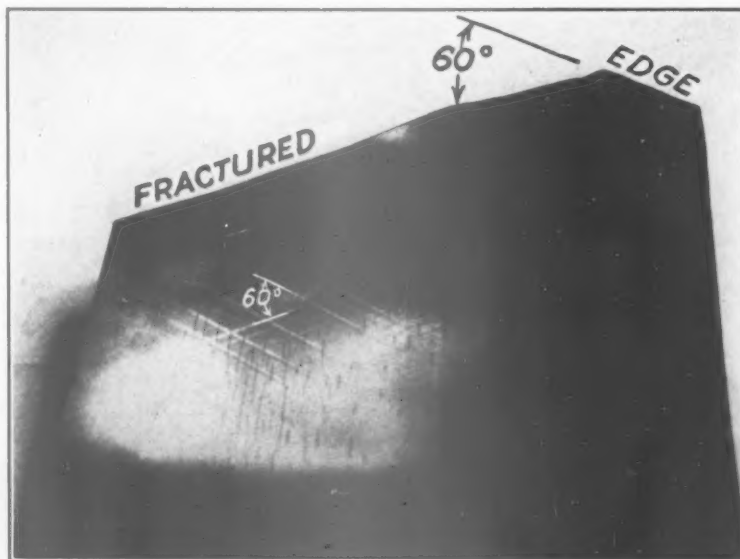


FIG. 35.—SHEET STRIP IS 7 BY 0.017 INCHES.

The authors have presented excellent experimental data on the nature of hydrogen embrittlement of iron and steel, and have ably explained these results by the imperfection theory of crystals—a viewpoint widely accepted among physicists.

No doubt the authors considered many other theories before accepting the imperfection theory as the most reasonable explanation of their results. In my opinion they are justified in doing so, for no other theory supports the facts better than the imperfection theory of the solid state.

It is admitted that our knowledge of the subboundary structure of grains is far from complete, though the field is being rapidly developed. Many theories have been presented, some of which have been abandoned or greatly modified since their introduction. In viewpoint many of these theories are not only divergent but often contradictory. This must not be interpreted to mean that the present state of confusion and uncertainty implies a fictitious nonexistent structural element within the grains, but rather expresses our lack of knowl-

edge of subboundary structure often referred to as a mosaic, block or group.

The experiments of Goetz¹¹⁵ on single crystals of bismuth strongly indicate that the block structure begins to form just before the metal is ready to solidify; in other words, the metal goes through some kind of paracrystalline phase just before it solidifies. This work has not received the attention it deserves; it is without question an outstanding contribution to our knowledge of the solid state, in that it explains why a crystal or grain is mosaic or contains a periodic block structure. When the "blocks" are perfectly aligned within the crystal it is said to be perfect, in that there are no interblock disjunctions; however, the "blocklike" structure exists inherently. The existence of a periodic structural unit is also well illustrated by cleaving a large single crystal of calcite into smaller units. This periodic structure is also exhibited when a single crystal of a ductile metal is slightly deformed, because equally spaced slip lines appear on the surface. This certainly proves

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¹¹⁵ A. Goetz: Experimental Evidence of Group Phenomena in the Solid Metallic State. *The Solid State of Matter*, London, 1934.

that some kind of periodic blocklike structure exists, because the shear strength varies and only certain planes slip while others remain intact. Further increasing the forces of defor-

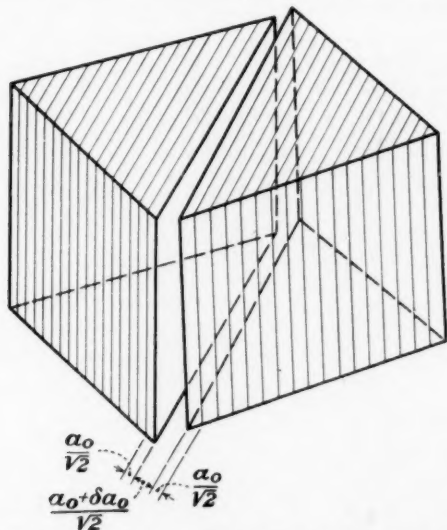


FIG. 36.—AN ATTEMPT TO PORTRAY THE MECHANISM OF DEFORMATION THAT A BLOCK UNDERGOES WHEN EXTERNAL FORCES EXCEED THE ELASTIC LIMIT.

THE MOVEMENT IS BOTH ROTATIONAL AND TRANSLATIONAL, WHICH CAUSES THE LATTICE SPACING AT THE DISJUNCTION TO INCREASE TO $\frac{a_0 + \delta a_0}{\sqrt{2}}$ (110 PLANES) AFTER DISPLACEMENT.

mation causes other planes to continue the slip, and so on until the limiting particle size is reached. The particles are then keyed together so that further deformation causes the material to part at the cleavage planes. X-ray evidence and other methods as well prove that the resistance to plastic flow does not occur with equal ease on all possible slip planes.

The blocklike structure of metals is also exhibited in Fig. 35, which shows the slip lines that were developed on the surface of a low-carbon strip steel, which fractured under rapid deformation in a single-stand Steckel mill. The strip was running at 1500 ft. per min. when the mill was suddenly stopped, with the resulting fracture. Previous to this the strip had received a reduction of about 30 per cent. This photograph is remarkable in that all of the slip planes bisect at 60° and not at 45° (ref. 50), as the maximum shear theory ascribes. The photograph cannot show the regularity with which the slip lines occur nor can it show the

depth of the lines. The regularity with which the lines occur substantiate a block theory, in that the blocks reached their maximum strength and keyed together before fracturing on the cleavage planes. Also, the fracture occurred on these slip planes and the intersection of the fractured edges make an angle of 60° . X-ray examination showed that these lines were parallel to the slip planes of the type (110). The lines running from top to bottom in the picture are guide marks and are not to be confused with slip lines.

Many experiments have been performed by various methods to learn more about the subboundary or imperfection structure of grains. Etch figures, Bitter patterns, the now classical X-ray diffraction studies of Darwin, and the method developed by the authors, all indicate that the "blocks" are about 10^{-5} cm. in magnitude.

The authors point out that the effect of both cold deformation and hydrogen absorption at the "block" disjunctions induce block displacement. These experiments discussed by the authors support the block-structure theory. It is conceivable that during the initial stages of hydrogen embrittlement and before the hydrogen pressure exceeds the elastic limit, the hydrogen must diffuse along a selective network of paths, which are more or less periodically spaced. In the final stages, however, when the pressure exceeds the elastic limit and fissures have formed, the network of hydrogen surrounds the limiting particle size.

The nature of hydrogen absorption by steel suggests that the grains possess a periodic block structure in which paths of varying resistance to hydrogen penetration exist, and the character of the fissures formed strongly suggest the existence of a periodic block structure.

X-ray diffraction methods (ref. 87) prove that the most drastic cold-working does not fragment the grains of alpha iron or steel without limit; the most drastic cold-working being capable only of reducing the grains of alpha iron into blocks of about 10^{-5} cm. in magnitude. Fragmentation of the grains into blocks proceeds by rotation and translation along the slip planes and becomes more and more difficult as the limiting particle size is approached. When this stage is reached the slip planes behave as though they were keyed and the

forces required to cause further slip may actually exceed the cleavage shear, with the result that numerous cracks begin to propagate throughout the grains and fracture finally occurs on these cleavage planes.

Furthermore, rotation of the "blocks" with respect to each other, as fragmentation proceeds, demands an increase in the spacing between the blocks, as indicated in Fig. 36. This will increase the internal surface and cause a slight decrease in the density. This theory appears to be consistent with the facts, for a single crystal has maximum density while a fine-grained annealed specimen has less density. Therefore, in a sense, cold-working reduces the grains into many smaller ones, and as a result the internal surface is increased and the spacing between the block disjunctions is also increased slightly by the rotation of the blocks.

In a previous paper (this volume, p. 272) X-ray evidence was presented (Fig. 11, p. 279) to show that plastic deformation in the early stages of flow involves the rotational displacement of large lattice blocks, and with continued working these are fragmented more and more into smaller ones until the limiting particle size is reached.

The same line of reasoning can be applied to hydrogen residing within the "block" disjunctions, as pointed out by the authors on page 227. When the pressure of the hydrogen exceeds the elastic limit of the material, block displacement by rotation takes place. The hydrogen finds the least resistance to its penetration around the blocks. This experiment by the authors seems to indicate that even in hydrogen embrittlement of iron a limiting particle size is associated with this phenomenon; for they point out that when the hydrogen is occluded about the blocks triaxially rupture occurs, since further slip is virtually impossible (see p. 231). This is the same as saying that a limiting particle size has been reached.

Apparently the occluded hydrogen cannot reduce the "block" size into smaller and smaller units without limit, the smallest "block" size being of the order of 10^{-5} cm. in magnitude, and therefore the mechanism of deformation is analogous to cold-working.

When the blocks are keyed triaxially, does rupture occur on the (110) slip planes or on the cleavage planes (100)? It may be that when

the limiting particle size has been attained the resistance to further flow on the slip planes may be so great that the forces that would cause further slip approach or exceed the cleavage strength.

The figures presented in this discussion were prepared by Mr. William Brenner, and the writer wishes to acknowledge his appreciation for this assistance.

D. P. SMITH,* Princeton, N. J.—The authors have given a stimulating discussion and valuable bibliography relating to defects in steel and their possible causation by hydrogen, in which they seek an explanation for embrittlement and other troubles in the existence of a block substructure within the metallic lattice, and the effects of hydrogen upon the disjunctions between the blocks. Apart from the well-known difficulties of the block-structure conception, set forth in some of the literature cited, there seem to the writer to be particular objections to just this explanation in the present connection. Blocks, in order that they may be blocks, must be completely surrounded by their disjunctions; and the result of the distention of such continuous disjunctions, by entry of hydrogen, should be not embrittlement, but disintegration. Yet iron and other metals absorb large quantities of hydrogen while still retaining a considerable part of their original cohesion. If the absorbed hydrogen is not uniformly distributed through the lattice, but is in large part concentrated, as much accumulated evidence seems to show, it would therefore appear that the regions affected are more localized than the supposed disjunctions of block structure, and are of a kind that interrupts the continuity of the lattice only here and there. Evidences that these regions are widenings of the lattice intervals, or small rifts, produced in the vicinities of the planes of slip by foregoing deformation, have been elsewhere considered (refs. 39, 40, 57, 69), and it may here be remarked only that such rifts, in incipient state, must of necessity be present in any metal that has undergone even slight plastic deformation, without subsequent recovery, if the view is correct that cold-work produces persistent changes in the atoms themselves. This view was reached, among others, by Tammann,¹¹⁶ as a result of the most extensive

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¹¹⁶ Reviewed in *Ztsch. Metallkunde* (1932) 24, 220-223; (1934) 26, 97-105; (1936) 28, 6-17.

studies of deformation yet conducted. Evidently altered atoms, with altered fields of force, entail disturbed atom planes, and interplanar spacings, which are widened in certain places. Such widenings, or rifts, if enlarged by hydrogen, are sufficient to account for embrittlement; and they need have no connection with a block structure, unless indeed such a structure is necessary to the occurrence of slip. They also appear to offer a readier explanation of some of the local defects, to which our authors refer, than would the continuous disjunctions of a mosaic. The comportment of hydrogen in iron and other metals, so far as it is yet known, seems to the writer to afford no evidence either for or against the existence of mosaic structures.

F. ZWICKY,* Pasadena, Calif.—A few supplementary remarks might be made on *secondary* and *mosaic structures*, and some additional references to the existing literature might be added for the benefit of those who wish to study the effects of occluded gases in metals from the viewpoint of the atomistic structure of matter.

To keep the nomenclature straight the following designations for deviations from the ideal crystal lattices in real crystals are recommended.

The *secondary structure*¹¹⁷ of real crystals consists of deviations from the ideal crystal lattices that are *thermodynamically stable* (absolute minimum of the free energy).

A *mosaic structure*¹¹⁷ of real crystals is due to the deviations from the ideal crystal lattice that are either *thermodynamically unstable* or at least *pseudostable* (secondary minimum of the free energy). A mosaic structure may have its origin in the deformation of an originally perfect crystal through the action of sufficiently large mechanical, thermal or electrical stresses. Or a mosaic structure may be formed immediately during the growth of the crystal. For instance, for crystals grown out of the melt a crystal may possess stratifications because of intrinsic changes of the speed of crystallization or the sedimentation of impurities, or there may be formed "frozen in" columnar vortices similar to some of the large-scale rock structures, well known to geologists, that consist of hexagonal

columns (such as the Devil's Post Pile in the High Sierra).

The problem of whether mosaic structures include all of the deviations in real crystals from the ideal crystal lattices or whether secondary structures exist even in the most perfect and thermodynamically stable crystals has not yet found an all-round satisfactory answer. For the question of hydrogen embrittlement as treated in the paper under discussion the controversy between the adherents of a secondary structure and the proponents of all inclusive mosaic structures is not at the present essential. It would be very illuminating, however, to conduct experiments on the hydrogen embrittlement of single crystals of iron. Starting from perfect single crystals and proceeding to crystals of increasing initial plastic deformation, the effects of occluded hydrogen on the various specimens might provide important information regarding the nature of secondary and mosaic structures.

For those interested in the subject under discussion the following references may be recommended.

The most beautiful stratifications (spacings about 0.8μ) were obtained by M. Straumanis¹¹⁸ in zinc and cadmium single crystals. Straumanis also showed first that on application of mechanical stresses slipping always occurs along the boundary lines of the equidistantly spaced blocks. An elegant theory of plastic deformations of this kind and the mechanical hysteresis effects related to it was given by P. Duwez.¹¹⁹ This theory is based on the concept of the existence of secondary structures in crystals and seems to be the most satisfactory theory given so far of irreversible mechanical deformations in crystals. This theory also may lend itself to a more quantitative discussion of the effects of occluded hydrogen on the mechanical properties of crystals. To provide the essential data for such a discussion it will be necessary to determine experimentally the effects of occluded hydrogen on the mechanical hysteresis curves of metal single crystals.

C. A. ZAPFFE AND C. E. SIMS (authors' reply).—Perhaps we should have made it clearer that the present paper is but a preliminary and incomplete unit of a subject that is being ex-

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¹¹⁷ F. Zwicky: *Proc. Nat. Acad. Sci.* (1929) **15**, 253, 816.

¹¹⁸ M. Straumanis: *Ztsch. physikal. Chem.* (1931) **13-B**, 316.

¹¹⁹ P. Duwez: *Phys. Rev.* (1934) **47**, 494.

tensively investigated at Battelle Memorial Institute. Archer points out that the observations recorded in this paper are consistent with the block theory, but do not verify it.

That is true. However, considerable proof for the theory has been obtained, and will be published shortly. Because that proof was slower in developing, and because the commercially occurring defects discussed in this paper had such obvious relationships and simple explanations without necessitating knowledge of the finer details of the substructure, we chose to take a temporarily dogmatic position on the strength of our unpublished results. Although a great amount of research will be needed to identify those finer details, enough evidence for the existence of substructural disjunctions is already at hand to make the conclusions of the present paper reasonable.

As a matter of fact, many of the observations discussed in the present work have already been well established by others and have been so widely accepted that certain criticisms raised in the discussion seem irrelevant. Especially surprising are Styri's remarks, for the sixteen-year-old work of Hultgren that he cites as authoritative antedates most of the important investigations on flakes and shatter cracks, which number in the hundreds¹⁰⁴ and which have proved to the published satisfaction of most European and American metallurgists that hydrogen is indispensable to the production of these defects. In the face of the mass of experimental evidence that has accumulated both here and abroad since Hultgren's work, there seems little plausible reason for doubting that hydrogen is necessary for flaking. *How* the gas operates, on the other hand, is moot, and it is to that consideration that the present paper is devoted.

Styri's comment "One gets the impression from a study of the paper, however, that . . . if it [hydrogen] was not present in sufficient quantities, such things as flakes and snowflakes could not occur" precisely summarizes the impression that we have endeavored to create. Rather than an impression, however, we believe it to be a general statement of fact, for it has been adequately demonstrated that without sufficient quantities of hydrogen in the steel such defects as flakes, snowflakes, shatter cracks, fisheyes, white spots, and similar defects, can hardly occur. The "hydrogen

bugaboo," again to quote Styri, is indeed real. That does not, of course, prevent cracking of the best and purest steel under extreme conditions of triaxial stress; but hydrogen-laden, hydrogen-embrittled locations crack under less severe conditions.

To speak of eliminating flakes by heat-treatment is to confuse the issue. They may only be prevented from occurring. A flake by accepted definition is a crack in the steel; obviously a crack need not heal during heat-treatment, although the pressure from forging should favor its healing. Heat-treatment only purposes to remove the embrittlement—not the crack.

Again, Styri apparently disregards the discussion on pages 250-258 on the behavior of hydrogen in steel during heat-treatment. There is no basis for believing that the slug he mentions, which had a thirtyfold greater cross section than the specimens in the present work, need lose sufficient hydrogen during the treatment he lists. Note the specimens in Figs. 26 and 33 that remained embrittled for 2 hr. at 700° and 800°C.; and in an unpublished test a 1/4-in. specimen remained embrittled after 24 hr. in vacuo at 1050°C.

How does Styri propose to explain fissures in steel on the basis of coarse grain size? Possibly Foley's comment on lower transformation temperature is applicable. Probably coarse grain size is simply a coincidental phenomenon and should not be used to confuse the explanation that hydrogen is, or was, present in the steel in excess; for hydrogen has been found to be a promoter of grain growth. That function of hydrogen is understandable, because some of those impurities that are thought to collect in grain boundaries and thereby inhibit grain growth react strongly with hydrogen and may be removed as gaseous compounds. Conversely, steel that is made under conditions favoring hydrogen absorption should show a minimum of the impurities that inhibit grain growth. In liquid steel hydrogen may act as a deoxidizer and desulphurizer.

For similar reasons, to attribute flakes to methods of hot-working or the presence of slag inclusions and blowholes, as Styri suggests, is much like blaming the gun instead of the bullet for the hole in the target. Admittedly, the processing may be conducted in a manner that will either produce or preclude flaking, but such

items are indirect agents and do not explain the defect.

Foley's comments are well placed. We are developing an apparatus for determining hydrogen in steel with which we hope to show that more accurate analyses can be made and that they will be consistent with practical observations. It is certainly true that extant data are unreliable and generally uninformative. On the other hand, one important reason for their apparent uselessness is the lamentable habit of expressing the analyses for that light gas in terms of weight per cent of iron; when, atom for atom, hydrogen requires thousands of times the space required by iron, and the effect of the gas on the iron is one of pressure and volume.

In regard to Foley's statement on the difficulty of reclaiming nickel ordnance steel by heat-treatment, we will point out that nickel markedly increases the solubility and changes the solubility relationships of hydrogen in steel; hence, the heat-treatment to which he refers may be open to question. Furthermore, such steels may often have a superabundance of hydrogen if they are made with electrolytic nickel, for cathode nickel may contain hundreds of times its own volume of that gas.

Cramer raises a question that is often heard, particularly in discussions on welding, but which has a simple and straightforward answer. To rupture without plastic deformation, a metal must either be embrittled or it must be stressed triaxially. In the case of hydrogen embrittlement both factors obtain. When steel containing hydrogen cools, the internal regions that collect sufficient quantities of the gas to become brittle will accordingly permit no accommodation of stresses except by rupture. In large forgings, internal stresses developing during cooling may require sufficient readjustment of the metal so that the portions that cannot flow will rupture. That rupture is the flake or shatter crack. In smaller sections such a major readjustment may never develop; and the embrittled region will remain *in status quo* until the hydrogen escapes or until an applied stress, such as from tensile testing, enforces movement that will rupture that region perpendicularly to the stress to display the characteristic shiny spot. Obviously, there must be an intermediate stage wherein moderate internal stresses may rupture the embrittled

zone, but in such a minor way that the direction of the break during tensile testing will still be determined by the applied tension. A flat-lying snowflake will then be observed as usual, although some additional small cracks may also be found throughout the embrittled zone.

In the particular case of weld metal, such as Cramer shows, there is another source of intrinsic stress that is characteristic of weld metal and is seldom found elsewhere. That is the long-distance stress from buckling or warping, which may be effective in addition to the local shrinkage stresses. The specimen Cramer presents very likely developed a silver-streak type fissure from just such an intrinsic stress and at a period sufficiently previous to the physical test that corrosion occurred in the meantime. In other words, that specimen simply represents a cracked weld; and the cracking in this case was apparently caused by a warping stress acting on hydrogen-embrittled metal that now shows as a corroded "silver streak." The other silver streaks and fisheyes visible on the fracture then formed during the imposed physical test, although some may also have formed earlier from intrinsic stresses but did not open to the surface. If the ones observed on the fracture did form before, however, it was a coincidence that the intrinsic stress operated in the same direction as the subsequently applied tension.

We do not yet have the answer to Epstein's questions regarding the yield point and blue-brittleness phenomena, although both are being considered for investigation.

To clarify the tests described on page 253, which were commented upon by Archer, it should be added that the 0.18 carbon steel was S.A.E. 1020 and that the tests were only to serve as qualitative illustrations. Quenching was adopted because hydrogen effusion during cooling was then a minimum and because the hardenability of S.A.E. 1020 steel is too slight to vitiate such qualitative results. The control specimens served as a further assurance that the measured changes in ductility were due principally to changes in the hydrogen embrittlement.

For many years Goss has been a proponent of the block-structure theory, while receiving little support from other metallurgists. In our supplementary publications we will present

evidence for substructure that stands in good agreement with Goss's reasoning. For those publications we will reserve discussion of his question regarding the crystallography of the hydrogen-embrittled fracture.

The researches of Smith and his co-workers have been of especial inspiration to us in developing a coherent and logical picture for hydrogen embrittlement in steel. Smith and his students have developed striking evidence that the occlusion of the hydrogen is crystallographic; but Smith apparently does not interpret his results as we do. In our opinion, a crystallographic feature is a fundamental feature of all the crystals; and to make an occluding rift a slip plane and at the same time to

suppose that the rift is localized and haphazard is to abnegate known facts. The precise spacing and pronounced crystallographic relationships of slip planes as evidenced by severely deformed metal support instead the present reasoning.

Zwicky's contribution we appreciate because he is the originator of one conception of crystal substructure and has pursued the argument energetically for many years. As Zwicky points out, to enter the argument over the details of the substructure is not pertinent at present; the fact that apparently there is some such fundamental characteristic of crystals demands investigation, and its recognition must bring many new conceptions to metallurgy besides the present one for hydrogen embrittlement.

Subboundary Structures of Recrystallized Iron

By N. P. GOSS,* MEMBER A.I.M.E.

(New York Meeting, February 1940)

ASTERISM appearing in X-ray Laue diagrams is an extremely sensitive index of changes in the internal structures of individual grains of polycrystalline metals. It indicates the existence of various forms of subboundary structure or subdivision within the grain. The present viewpoint is that the grain is made up of lattice blocks having substantially the same size and shape.¹⁻⁴ When these blocks all assume exactly the same orientation, the crystal is perfect and asterism is absent.

Cleaves and Thompson⁵ observed that the hardness of iron is virtually constant over a range of grain sizes. It is quite possible that the subboundary structure caused this, and that the latter is just as important as grain size itself. While the experiments reported here are not conclusive, they do support this viewpoint.

Metals can, under certain conditions, be prepared entirely free from asterism, but this preparation does not necessarily require long heating or slow cooling, as will be shown here.

In this paper a distinction is made between mosaic and distorted grain structures but the difference is only a matter of degree. In a previous paper⁹ it was shown that the grains can become distorted even during heat-treatment. The block structure exists inherently, even in a perfect crystal; the size and shape of these crystallites, or lattice blocks, varies, depending upon a number of factors. Goetz, for example,⁷

has shown that a metal before crystallizing from the molten state must go through a paracrystalline phase with oriented groups of atoms about 10^{-14} to 10^{-15} c.c., or 10^{-5} cm. in size.

These crystallites, or blocks, appear to survive the most drastic cold-working, for it has been shown, and more elaborately by Wood's recent work,¹¹ that cold-working cannot reduce the size of these crystallites smaller than of the order 10^{-5} cm. The interesting correlation brought out by the experiments of Goetz and Wood is that the block size after severe cold-working is of the same order of magnitude as the groups that formed in the metal just before crystallizing from the molten state.

The work of Ewald and Rennenger¹⁷ and the now classical experiments of Darwin and James^{12,13} all strongly suggest the existence of a periodic structure of crystallites smaller than the grain itself. Related to this effect is the appearance of veinlike markings in the microstructures. Ammerman and Kornfeld,¹⁶ in their experiments, did not observe any evidence of veining in specimens of alpha iron annealed below A_3 and believed that veining was not due to impurities in the iron, as Northcott¹⁸ suggested; veining was observed by them only in specimens annealed above A_3 . Hanemann,¹⁶ Schrader and Tangerding found that annealing in hydrogen did not diminish veining and so it could not be caused by oxides. They concluded that veining was due to a slight difference in the orientation of ferrite lattice blocks. This viewpoint is well supported by the evidence presented here.

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* Physicist, Cold Metal Process Co., Youngstown, Ohio.

¹ References are at the end of the paper.

EXPERIMENTAL PROCEDURE

Ingot iron (analysis, 0.04 C, 0.017 Mn, 0.006 P, 0.020 S) in the form of hot-rolled strip was cold-rolled from 0.076 to 0.048 in.

content well under 0.02 per cent. It was found by experiment that large crystals could be grown when the strip had been annealed above A_3 before critical straining.

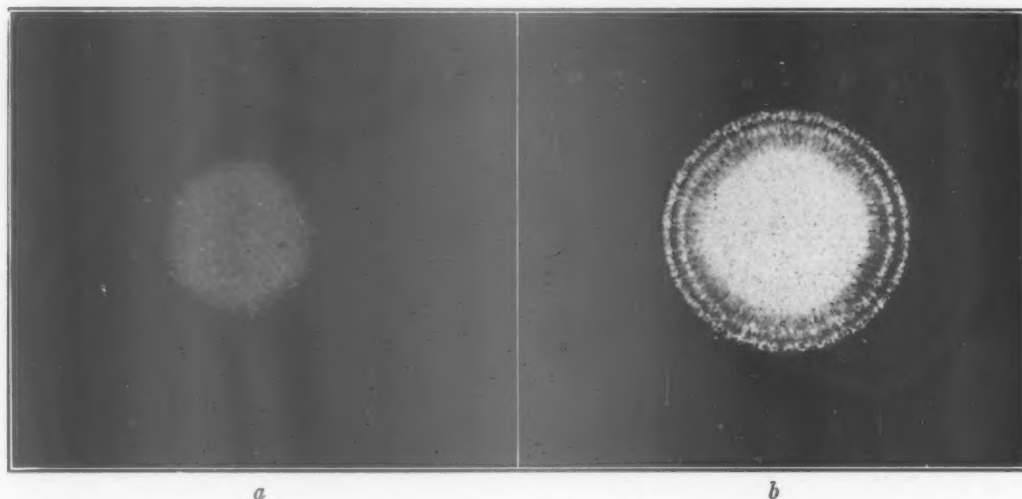


FIG. 1.—X-RAY LAUE DIAGRAMS OF CRYSTALLINE AGGREGATES IN WHICH GRAINS ARE SUBSTANTIALLY PERFECT AND MOSAIC. IN PERFECT GRAINS LAUE SPOTS ARE SHARP. IN MOSAIC STRUCTURE LAUE SPOTS EXHIBIT ASTERISM AND ARE ILL DEFINED.

a. Fine-grained pure iron 0.004 inch thick (cold-rolled from 0.060 to 0.004 inch). Annealed at 1480°F.

b. Same as a but annealed at 1700°F.

annealed above A_3 in a reducing atmosphere (containing about 8 per cent hydrogen) for 24 hr. and slowly cooled in the furnace, reaching room temperature in about 15 hr.

TABLE 1.—Hardness Tests on 0.048-inch Strip Critically Strained and Annealed at 1500°F.

Grain Size, Diameter, In.	Rockwell, 30/T	Position
$\frac{1}{4}$ (one grain only).....	34-36-33	Near boundary of grain
	41-39	Center of grain
$\frac{1}{8}$ to $\frac{1}{32}$	30-27-30	Strip No. 1
	31-26	
$\frac{1}{32}$ and under.....	35-37-39	Strip No. 2
	38-35-39	

The strips were then critically strained by cold-rolling (1 to 5 per cent) and annealed at 1500°F. for 36 hr. in the same reducing atmosphere and slowly cooled. The reducing atmosphere prevented oxidation of the strip and further decreased the carbon

The grains varied from $\frac{1}{64}$ in. to over 1 in. in diameter but only strips having a grain size $\frac{1}{4}$ in. or under were used in this experiment. The Rockwell hardness numbers of these strips are given in Table 1.

Apparently there is no relationship between the hardness value and grain size in this range.

Some of these strips were cold-rolled to various gauges, ranging from 0.004 to 0.022 in., without any intermediate annealings, on a two-high laboratory cold-rolling mill. Before cold-rolling, the strips were etched in a 10 per cent Nital solution to bring out the grain structure, which could be seen with the naked eye. After cold-rolling, the elongated grains could be observed.

For X-ray examination these were cut, prior to heat-treatment, into a number of small pieces suitable for examination by the Laue method. Some of these X-ray specimens were heat-treated above A_3 and

others below A_3 (1300° to 1500°F.) for various annealing times and under different conditions of heating and cooling. To protect the specimens from oxidation during

of the specimens for X-ray examination by the Laue method is of the greatest importance—the slightest bending other than elastic will fragment the grains mechanically.

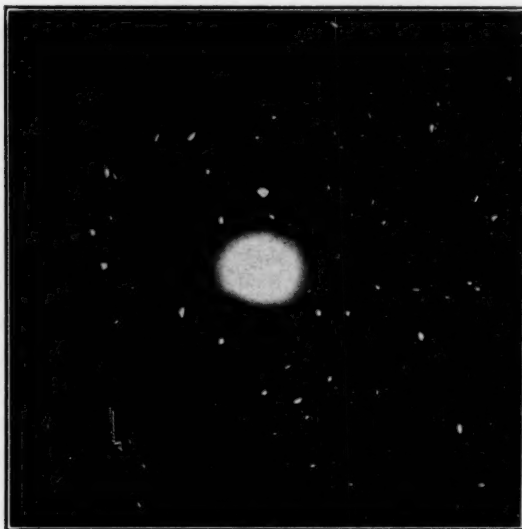


FIG. 2.

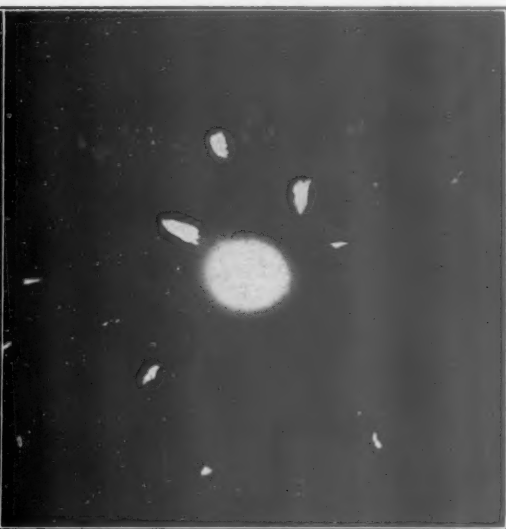


FIG. 3.

FIG. 2.—X-RAY LAUE DIAGRAM OF PURE ELECTROLYTIC IRON AS DEPOSITED, 0.010 INCH THICK.

This strip was annealed at 1300°F. for 12 hours and slowly cooled in the furnace. This specimen was X-rayed without preparation. Grains are only slightly distorted.

FIG. 3.—X-RAY LAUE DIAGRAM OF PURE IRON ANNEALED AT 1500°F. AND SLOWLY COOLED IN FURNACE.

This diagram shows that grains were distorted by rotation of large lattice blocks relative to each other. The diffuseness of striations in elongated Laue spots indicates that displaced lattice blocks are mosaic.

annealing, they were carefully wrapped in a protective sheathing of thin strip steel.

The annealed specimens were etched in a 20 per cent Nital solution to bring out the grain structure. The elongated grain boundaries still persisted in the strips annealed below A_3 but were completely obliterated in the specimens annealed above A_3 .

The source of X-ray radiation was a Coolidge tube with a molybdenum target, operated at 35,000 volts and 15 ma. The X-ray beam was defined by two pinholes 0.025-in. diameter and 3.5 in. apart. The specimen was placed over the pinhole nearest the plate holder, therefore the specimen and film were 2 in. apart.

Specimens thicker than 0.008 in. were etched to this thickness. The preparation

The microscopic specimens of the cold-rolled strips were cut before heat-treatment and after heat-treatment were mounted in Lucite. Repeated etching in 1 per cent Nital or a 5 per cent Picral solution and polishing was required to bring out the subboundary structure, the technique due to Vilella⁶ being followed.

EXPERIMENTAL RESULTS AND DISCUSSION

Very little distortion is observed in Laue diagrams of thin strips of cold-rolled ingot iron or pure iron heat-treated below A_3 . The diagram of Fig. 1a illustrates this type of structure. This pure iron was cold-rolled from 0.060 to 0.004 in. and annealed at 1480°F. The Laue spots are sharply defined, therefore these grains are quite

perfect. On the other hand, when this cold-rolled pure iron was annealed above A_3 the grains were distorted and the Laue spots exhibit asterism and lack sharpness as in Fig. 1b. Some of the spots are more diffuse than others, which shows that the structure is not a homogeneous mosaic structure. In such a structure the lattice blocks, or crystallites, differ slightly in orientation. When a beam of X-rays is reflected from such a surface of atom planes the image of the focal spot cannot be sharply reflected but becomes slightly blurred. This type of asterism is caused by the reflection of the characteristic radiation and in some instances "white radiation" over a small range at the Bragg angle.⁷⁻⁹

Fig. 2 is a Laue diagram of a strip of pure electrolytic iron 0.010 in. thick, heat-treated at 1300°F. for 12 hr. and slowly cooled in the furnace. Asterism can be observed on many of the Laue spots, indicating only slightly distortion. This Laue diagram proves that slow heating and long time annealing and slow cooling does not always produce perfect crystals, or grains.

Fig. 3 is presented to illustrate a severely distorted grain structure developed during annealing. This specimen of iron was annealed at 1500°F. and slowly cooled in the furnace. The X-ray beam was transmitted through what appeared to be a single grain. It was rather surprising to find so much distortion in a slowly cooled specimen. Apparently relatively small forces that may arise during heat-treatment can, in some instances, distort the subboundary structure. The Laue spots of Fig. 3 are clearly striated, which shows that the displaced blocks are fairly large and consist of a large number of the fundamental crystallites. The radial streaks are due to the reflection of "white radiation" and the characteristic radiation from crystal faces differing slightly from each other, but the total deviation may be several degrees of arc. The individual stria-

tions appear diffuse, which proves that these large lattice blocks are mosaic.

Experiment showed that substantially perfect grains can be developed in silicon



FIG. 4.—X-RAY LAUE DIAGRAM OF SINGLE CRYSTAL OF 3 PER CENT SILICON FERRITE.

The cold-rolled strip was heated rapidly to 2000°F. and held at that temperature to permit grain growth, then rapidly cooled in air.

ferrite (Fig. 4). The diffraction maxima are sharply defined and free from asterism. The excellent magnetic properties of this material is in part, at least, due to perfect crystal structure. This structure was developed by heating the drastically cold-rolled 3 per cent Si ferrite rapidly to 2000°F. and holding at this temperature for a time sufficient to permit grain growth and then cooling rapidly in air. The interesting point brought out here is that rapid heating and cooling did not cause grain distortion.

The strips of ingot iron that had been cold-rolled to various gauges ranging from

0.010 to 0.022 in., as previously described and heat-treated above A_3 , were examined by the Laue method. A Laue diagram typical of this group shown in Fig. 5

defined as in Fig. 4. The grains therefore are built up of smaller crystallites, which differ gradually in orientation from each other. The striated structure of some of the



FIG. 5.—LARGE-GRAINED INGOT IRON, COLD-ROLLED FROM 0.048 INCH TO 0.012 INCH AND HEATED TO 1700°F. AND AIR-QUENCHED.

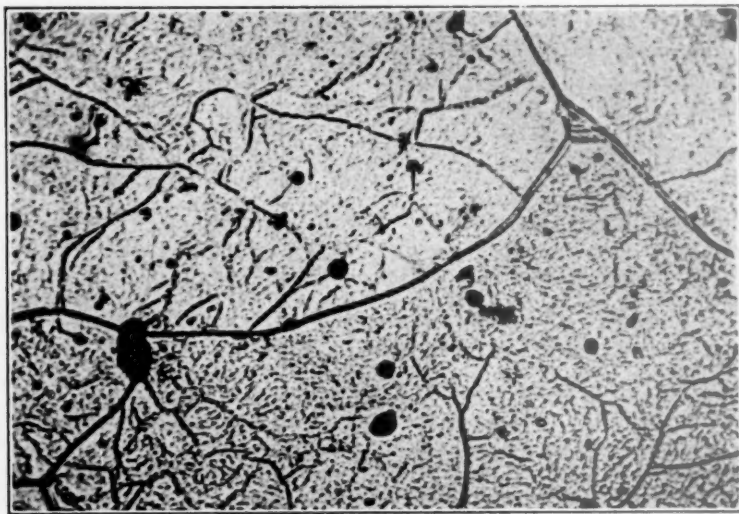


FIG. 6.—MICROSTRUCTURE OF STRIP OF INGOT IRON HEATED ABOVE A_3 AND COOLED RAPIDLY. $\times 500$.

Veining is found only in specimens that exhibit asterism. It is due to grain fragmentation that occurs during heat-treatment and may be due to various causes. Here it is caused by the gamma to alpha transformation.

(0.012 in. thick) shows that the grains are fairly large but the Laue spots are elongated and distorted instead of sharply

Laue spots shows that some of the displaced crystallites are fairly large.

The microstructure representative of

this group of specimens is shown in Fig. 6. These grains exhibit a subboundary structure usually referred to as veining.⁸ The well-defined grain boundaries shown in

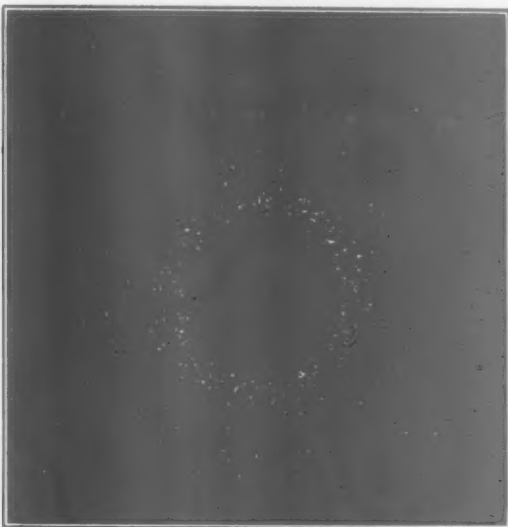


FIG. 7.—LAUE DIAGRAM OF INGOT IRON COLD-ROLLED FROM 0.048 INCH TO 0.011 INCH AND ANNEALED AT 1500°F. AND AIR-QUENCHED.

The Laue spots do not exhibit asterism and are surprisingly sharp.

Fig. 6 outline the parent austenitic grains from which the grains of alpha iron have formed. The austenitic grain boundaries persist even though the gamma iron has completely transformed into alpha iron. The single grain of austenite, however, as a result of the transformation, has been fragmented into a large number of smaller crystallites of alpha iron, which differ slightly in orientation from each other, and the crystal faces are all of the same family, while the faces on different grains are of various crystal planes; however, these crystallites are much larger than the smallest possible, which is of the order 10^{-5} cm. The internal network, or veining, outlines in a rather ill-defined manner the boundaries between the slightly displaced crystallites of alpha iron. It may be assumed, therefore, that asterism and veining are related. It remains to be shown, however, that veining is not observed in specimens that do not exhibit asterism. The

following procedure was used to establish this point.

Strips of ingot iron, less than 0.015 in. thick, were heat-treated at 1500°F. for

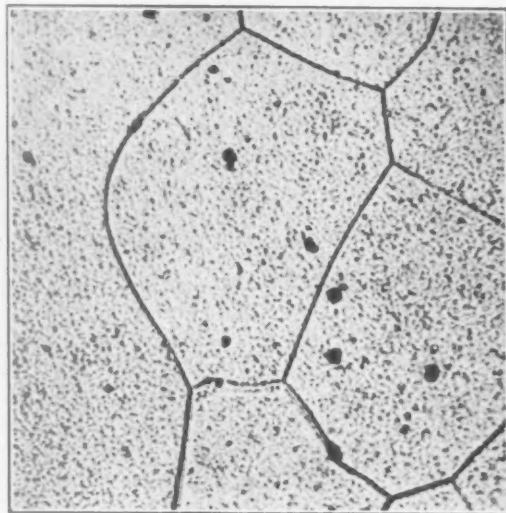


FIG. 8.—MICROSTRUCTURE OF SPECIMEN SHOWN IN FIG. 7. $\times 500$.

These grains did not exhibit veining. This proves that asterism and veining are related.

1 to 3 min. and cooled rapidly in air, and in spite of the rapid cooling a nearly perfect crystal structure was developed. A structure representative of this heat-treatment is shown in Fig. 7. The Laue spots are surprisingly sharp and well defined and free of asterism.

Fig. 8 is a microstructure typical of a large group of specimens free from asterism in which deep etching failed to reveal any evidence of veining. The evidence presented indicates strongly that Laue diagrams that do not exhibit asterism will not show veining in the microstructure.

So far it has been shown that when the strips are thin enough grains free from distortion or veining can be produced when annealed below A_3 , as in Fig. 1a. However, when the thickness of the strips of alpha iron was sufficiently increased it became more and more difficult to grow perfect crystals even below A_3 . The Laue diagram and microstructure shown in Figs. 9 and 10 show that large grains grown by annealing



FIG. 9.

FIG. 9.—LAUE DIAGRAM MADE OF ANNEALED STRIP OF INGOT IRON. The hot-rolled strip was cold-rolled from 0.079 to 0.048 inch and annealed above A_3 and critically strained, then annealed at 1300° to 1400°F. for 12 hours and slowly cooled in the furnace. Grains are distorted and microstructure, Fig. 10, indicates that well-developed veining is associated with a high degree of asterism.

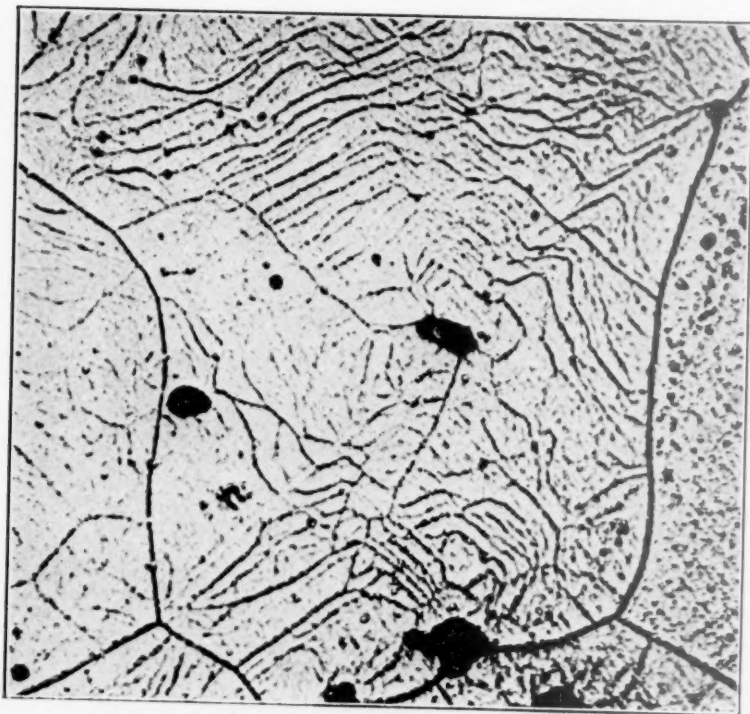


FIG. 10.

FIG. 10.—MICROSTRUCTURE OF MATERIAL SHOWN IN FIG. 9. $\times 500$. Grains exhibit subboundary structure. Veining predominates, but slip lines also appear to be present.

critically strained alpha iron below A_3 can become distorted during growth. This strip was 0.048 in. thick, heat-treated at 1500°F. for 12 hr. and slowly cooled in the furnace.

of growth these grains as well as the growing grains may become distorted.

To distort grains during heat-treatment, it is only necessary that the forces causing



FIG. 11.—THIS SINGLE GRAIN OF INGOT IRON WAS GIVEN A SLIGHT PLASTIC DEFORMATION (LESS THAN 1 PER CENT), WHICH FRAGMENTED THE GRAINS INTO SMALLER UNITS.

Even though the deformation was very slight, the lattice blocks appear to be displaced several degrees of arc, which is surprisingly large. This is shown by the splitting of the Laue spot into a number of elongated striations. These striations do not appear sharp, but diffuse and are interpreted to indicate a mosaic structure.

Slow cooling and long-time annealing did not prevent grain distortion. Fig. 10 is the microstructure of this material. It exhibits veining and perhaps slip lines as well. The distortion of the grains was developed according to the mechanism¹⁰ already described in a previous paper:

When a crystal or grain in its state of growth, assuming for the moment that it is growing freely in all its selective crystallographic directions, encounters other grains not in the state of growth, or grains unsuitably oriented relative to it for absorption, external forces (forces of constraint) resisting its growth are set up. If these forces of constraint exceed the tendency of growth of the grain further growth ceases. Also if the forces set up by the growing grain exceed the external forces set up by the surrounding grains whether or not in the state

grain growth and forces of constraint exceed the elastic limit of the grains at the recrystallization temperature. It should be pointed out that very little is known about these forces that are set up during recrystallization, but the effect on the crystal structure can be observed. Very little is known about the effect of the subboundary structure on the physical properties of perfect and imperfect grains.

Further proof of the existence of a more fundamental unit smaller than the grain is best illustrated by observing what happens to the grains when they are slightly strained (Fig. 11). A large single crystal of alpha iron about 0.010 in. thick was used. The Laue pattern of the undeformed grain was similar to the one shown in Fig. 2, in which several of the Laue spots ex-

hibited slight asterism. The specimen was then slightly deformed, less than 1 per cent, by cold-rolling. The Laue diagram after this deformation shows that lattice blocks were displaced relative to each other by rotation. The displaced blocks are fairly large and the degree of rotation is surprisingly large. In other words, the deformation does not proceed by a uniform displacement upon all possible slip planes, but large rotational displacements take place between very large lattice fragments of the order 10^{-4} cm. The diffuseness of the individual striations shows that the deformation was carried far enough to cause very slight displacements within the large blocks themselves. This evidence is believed to support the existence of a subboundary structure within the grain, and to give further proof that plastic deformation is not homogeneous.

SUMMARY

1. Subboundary structures indicated by asterism in Laue diagrams are common in alpha iron and are found to result from strains produced either by the gamma-alpha transformation or by forces that cause recrystallization and subsequently grain growth.
2. Thin strip is less likely to exhibit asterism than thicker material.

3. In some instances the rate of heating and cooling has little effect on the structure.

4. Veining is observed only in the microstructure of samples showing well-developed asterism.

5. Laue diagrams of single crystals deformed less than 1 per cent clearly reveal the existence of subboundary structure, and show that the deformation is not homogeneous.

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Analysis of the Cold-rolling Texture of Iron

By CHARLES S. BARRETT,* MEMBER AND L. H. LEVENSON,† JUNIOR MEMBER A.I.M.E.

(Cleveland Meeting, October 1940)

NUMEROUS determinations¹⁻⁷ of the texture of cold-rolled polycrystalline iron, steel, and ferritic alloys have been made with good agreement among the various observers as to the principal features of the texture common to all, but there has been no adequate explanation of the texture in terms of the behavior of individual grains. This study presents an explanation of the texture based on the observed rotation of single crystals when deformed in a manner similar to a grain in the aggregate, a method we have found useful in leading to a better understanding of compression and tension textures;^{8,9,10} in particular, the aim has been to determine experimentally the end orientations of rolled single crystals of iron. These are discussed in connection with the point of view of Wever¹ and of Boas and Schmid² that the rolling texture is a simple compression texture (compression normal to the rolling plane) superimposed on a simple tension texture (tension in the rolling direction), and the point of view of Kurdjumow and Sachs³ that three ideal end orientations exist.

EXPERIMENTAL METHOD

The single crystals used were in the form of disks cut from a stock of crystals† prepared in this laboratory by a strain-anneal method from mild steel decarburized and purified in hydrogen, the details of which have been described elsewhere.¹¹

To ensure maximum elongation in the rolling direction and to simulate approximately the rolling of a grain in an aggregate, lateral flow was constrained by placing each crystal in a close-fitting hole in a plate of copper or iron of equal thickness and rolling the plate and crystal together. About one-third of the crystals were rolled in a "sandwich" pack by adding top and bottom cover plates. The two-high mill used had 8-in. diameter rolls and was operated at 15 r.p.m. The initial diameter of the crystals was between $\frac{1}{4}$ and $\frac{1}{2}$ in., while the starting thickness varied from 0.031 to 0.376 in. With a single exception, which was rolled 63 per cent, the crystals were rolled to a final reduction in thickness of 82 to 97 per cent in 20 to 40 passes, alternately changing the sense of the rolling direction.

The initial orientations of the crystals were determined either by X-ray back reflection¹² or by optical reflection¹³ from etch pits; the mean final orientations were determined by X-ray Laue photograms using molybdenum, silver, or tungsten radiations, by optical reflection, and in many cases by both methods.

RESULTS

Twenty-six crystals were studied. It was found that there were three typical be-

included grains affected the rotation of the material only in their immediate vicinity, a negligible fraction of the total volume of material.

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¹ References are at the end of the paper.

‡ The single crystals contained a number of small included grains of the order of 0.1 mm. in diameter, which were found to be oriented as twins of the parent crystals, but these occupied less than one per cent of the total volume. From the appearance of the etched surface after rolling, it seemed obvious that the

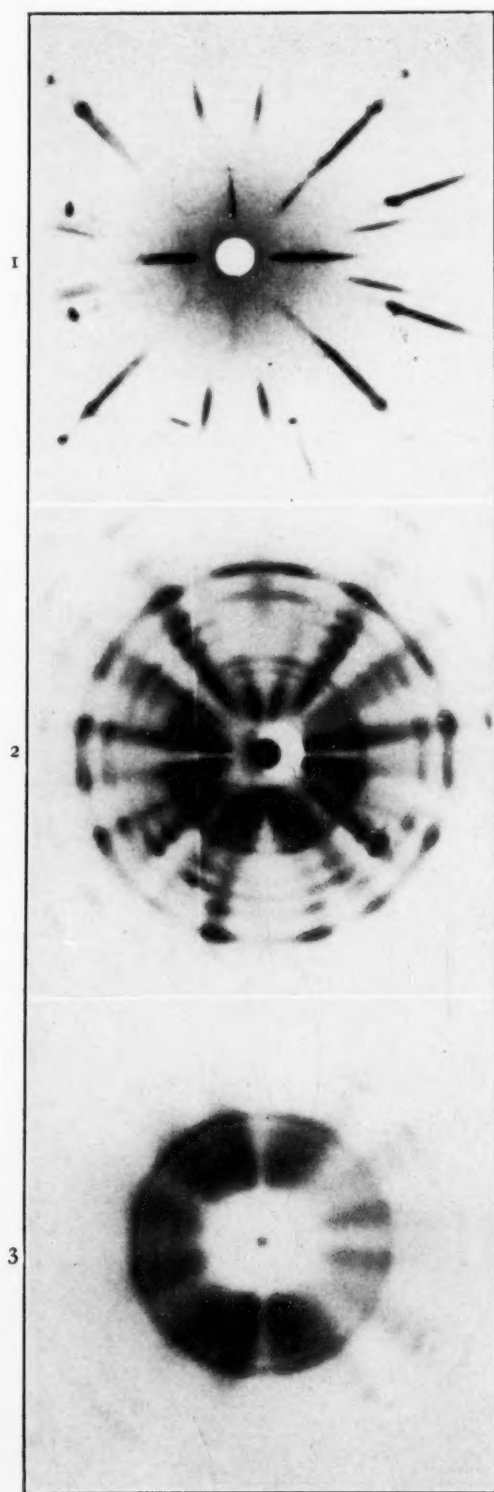


FIG. 1.—TRANSMISSION LAUE PHOTOGRAPH OF CRYSTAL 15-3 AFTER 95 PER CENT REDUCTION. Rolling direction vertical. Beam 90° from

haviors. Depending on the initial orientation of both the normal and rolling directions, some of the crystals (designated here, for convenience, as class 1) maintained or rotated into a reasonably sharp single orientation during deformation; others (class 2) rotated into two distinct orientations by the formation of fragments or of deformation bands, while still others (class 3) fragmented into a large number of major and minor orientations, sometimes approaching the entire polycrystalline pole figure.

Fig. 1 shows the transmission Laue photograph of crystal 15-3 after 95 per cent reduction in thickness, as an example of the first class. The film was taken with the beam 90° from the rolling direction, which is vertical, and 68° from the rolling plane, a setting that yields cubic symmetry and proves that the beam is parallel to the mean position of a cubic axis. Since the spread indicated in the photograph is of the order of $\pm 10^\circ$ around the rolling direction (vertical), about half this around the transverse direction, and only about $\pm 2^\circ$ around the normal direction, it is clear that the disk has remained a pseudo-single crystal throughout a 95 per cent reduction in thickness.

As an example of double rotation, class 2, the transmission Laue photograph of disk D-7 after 92 per cent reduction is shown in Fig. 2. Although the spread is fairly large, the pattern may be resolved into two distinct mean orientations, which are approaching two different orientations of the type $(001) [110]$.*

* The indices in parenthesis indicate the rolling plane; those in square brackets indicate the rolling direction.

rolling direction and 68° from rolling plane. Example of class 1, single final orientation.

FIG. 2.—LAUE PHOTOGRAPH OF CRYSTAL D-7 AFTER 92 PER CENT REDUCTION.

Rolling direction vertical; rolling plane in plane of paper. Example of class 2; double final orientation.

FIG. 3.—LAUE PHOTOGRAPH OF CRYSTAL 15-1 AFTER 92 PER CENT REDUCTION.

Rolling direction vertical; rolling plane in plane of paper. Example of class 3, multiple final orientation.

Multiple rotation, class 3, is illustrated by crystal 15-1 whose transmission Laue photograph after 92 per cent reduction is shown in Fig. 3. Here the Debye rings are

deformation bands. Crystal 15-1 is shown only in its initial position, with R.D. at 6 o'clock; it is representative of class 3. A series of X-ray films was made

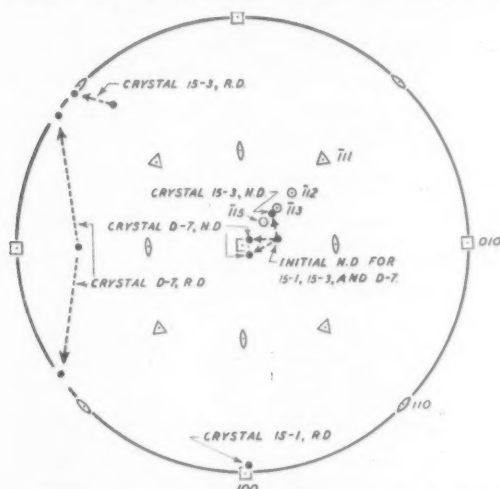


FIG. 4.—STANDARD PROJECTION OF INITIAL AND MEAN FINAL ORIENTATIONS OF CRYSTALS OF FIGS. 1, 2 AND 3.

N.D. is the normal direction; R.D. is the rolling direction. Dashed arrows point from initial to final positions (but do not indicate exact path followed).

continuous with a complex distribution of maxima indicating a large range of orientations of various intensities. The rotations of these crystals are plotted in the standard projection of Fig. 4. Three crystals are plotted in this figure with initial normal directions identical, indicated by "Initial N.D." near the center of the projection, but with different rolling directions, "R.D." Dashed arrows lead from the initial to the final positions but are not intended to indicate the exact path followed. Crystal 15-3, class 1, with R.D. near 10 o'clock on the figure, rotated to a single final position, the rolling direction rotating toward the closest $\{110\}$ pole and the normal direction toward $[\bar{1}13]$. Crystal D-7, of class 2, with its initial R.D. at 9 o'clock in the figure, split into two orientations, ending at 8 and 10 o'clock. The symmetrical position of its initial R.D. midway between two $\{110\}$ poles probably accounts for its breaking up into differently rotating fragments or

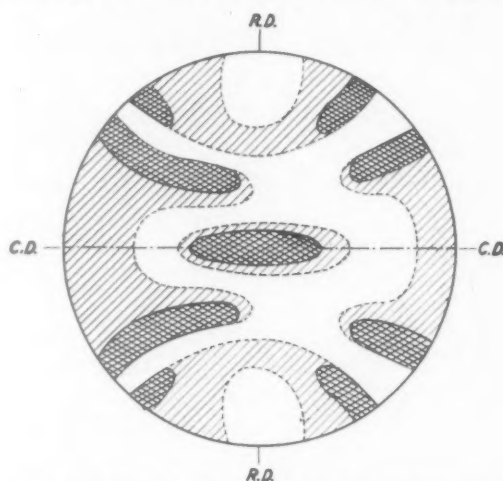


FIG. 5.—CUBE POLE FIGURE FOR CRYSTAL 15-1 AFTER 92 PER CENT REDUCTION.

using silver radiation, with the crystal 15-1 rotated 180° about the rolling direction in 10° intervals, and the pole figure for $\{100\}$ planes shown in Fig. 5 was prepared. It appears fairly obvious, by comparing

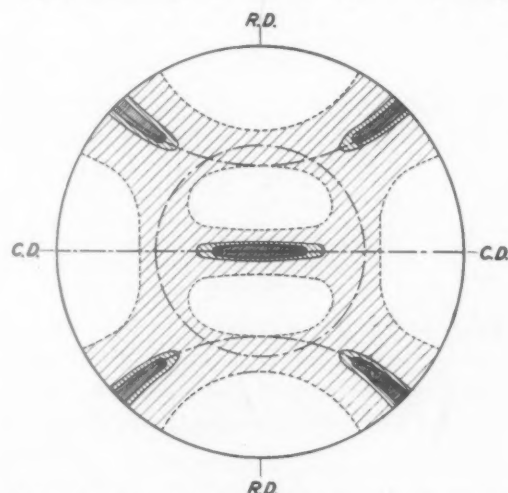


FIG. 6.—TYPICAL CUBE POLE FIGURE FOR ROLLED POLYCRYSTALLINE IRON.

Fig. 5 with a typical cube pole figure for rolled polycrystalline iron⁴ (Fig. 6) that the crystal is approaching the polycrystalline pole figure as a limit. The symmetry of the initial orientation (Fig. 4) would lead one

to expect a large number of rotations, since the rolling direction is approximately equidistant from four {110} poles and the normal direction is close to a plane of symmetry.

The experimental data are summarized in Table I, which gives for each crystal the initial thickness and orientation, the mean final orientation (when this has been determined), the total reduction in thickness,

than 10° away, toward which the crystal lattice appears to be rotating or about which it is spreading. No special significance is attached to these particular six end orientations, for, as discussed in the next section, they appear to be merely representative members of two continuous sets of orientations; they have been chosen somewhat arbitrarily for convenience in labeling the observed final textures.

TABLE I.—Summary of Experimental Data

Crystal	Initial Thickness, In.	Reduction in Thickness, Per Cent.	Initial Orientation						Mean Final Orientation						Class	Description
			Normal Direction (N.D.), Degrees from			Rolling Direction (R.D.), Degrees from			Normal Direction (N.D.), Degrees from			Rolling Direction (R.D.), Degrees from				
			[100]	[110]	[111]	[100]	[110]	[111]	[100]	[110]	[111]	[100]	[110]	[111]		
10-1	0.100	88	7½	38½	47	44½	2	33½	14½	36	40	41½	3½	35	1	(115) [110]
10-2	0.100	87	6½	39	49	2	43	54							3	
10-3	0.072	88	5½	40½	50	26½	19	40	13	33½	43	43½	4½	31	1	(115) [110]
10-4	0.072	89	3	42½	52½	18½	26½	43	15½	35½	39½	42	3½	34	1	(115) [110]
11-1	0.123	89	41	4½	33½	3	42	52½	49	29½	6½	41½	27½	13½		
									49½	30	6½	35	27	20	2	(111) [211]
11-2	0.123	88	41½	4½	33	41½	3½	35½							3	
11-3	0.123	90	42½	4	33	52½	31	4	32	26	23	45	5	30	1	(112) [110]
11-4	0.123	90	42½	4	33	35½	26	20	32½	29½	22½	42	3½	35	1	(112) [110]
12-1	0.224	91	47½	29½	8	45	4	31½	37	28	18	45	3	32½	1	(112) [110]
12-2	0.224	97	46½	29	8½	33	29½	22½							3	(111) [211]
13-2	0.152	94	42	22	16	49	32	6	39½	30	15	41½	6	31½	1	(112) [110]
14-1	0.152	96	42½	28	13	42½	2½	34½	43	27	12½	42	8½	28	1	(112) [110]
14-2	0.152	94	42	29½	13½	49	32	5½	49½	33	5	35½	16	26	1(?)	(111) [110]
15-1	0.376	92	18½	26½	41	2	43	53½							3	
15-2	0.376	92	19	25½	41½	19	26	42							3	
15-3	0.376	95	18½	27	41	43½	11½	25	22½	33	32½	42½	2½	34½	1	(113) [110]
D-2	0.035	82	29½	15½	35½	42	29½	13	15	35½	39	43½	1½	34½	1	(115) [110]
D-4	0.032	82	30½	27	25	30½	24½	25½	19½	32½	35½	39	6½	33	1(?)	(115) [110]
D-5	0.031	87	34	18½	25½	44½	26	12	2	43	52½	41	4½	33½	1	(001) [110]
D-6	0.034	83	12	33	46½	37½	10½	29	1½	43½	54	43½	1½	35	1	(001) [110]
D-7	0.037	92	18½	27	40½	18	27	43½	4	42	51	35½	9½	35		
									6½	40	49	35	10	36	2	(001) [110]
D-8	0.038	63	38½	16	23½	37½	28	17½	42½	22½	15½	38	23	18	1	
D-10	0.036	83	31	14	37½	31	14	37½							3	
D-11	0.036	86	31½	14	34	40½	27½	14½							3	
D-13	0.091	82	51	29	6½	39½	6	33½	43	24½	14	45½	10	25½	1	(112) [110]
D-14	0.114	88	52½	33	3	34½	30½	20							3	(111) [211]

and the classification into one of the three classes discussed above. There is no sharp dividing line between classes 2 and 3, owing to the wide range of orientations frequently encountered. We have adopted this scheme of classification as a substitute for working out pole figures for each crystal, which would be a laborious and cumbersome procedure of doubtful value. In the last column on the right, the mean final rolling plane and direction are indicated by one of six pairs of crystallographic planes and directions of low indices which are not more

In Fig. 7a are plotted the initial positions for the cube poles (three cube poles for each crystal) of all the crystals whose final orientations have been listed in Table I (19 in all); these appear as dots superimposed on the polycrystalline pole figure as a background. Each orientation has been plotted in four equivalent positions using the rolling and cross directions as lines of symmetry. While the distribution of poles is not entirely uniform, it covers most of the projection and many of the poles lie outside the shaded areas of the polycrystal-

line pole figure. The mean cube poles of the same crystals after rolling are plotted in Fig. 7b; all crystals whose poles originally were within the unshaded areas of the poly-

the rolling plane and rolling direction of the following types: (A), (001) $[\bar{1}10]$; (B), $(\bar{1}15)$ $[110]$; (C), $(\bar{1}13)$ $[110]$; (D), $(\bar{1}12)$ $[110]$; (E), $(\bar{1}11)$ $[110]$; (F), $(\bar{1}11)$ $[211]$.

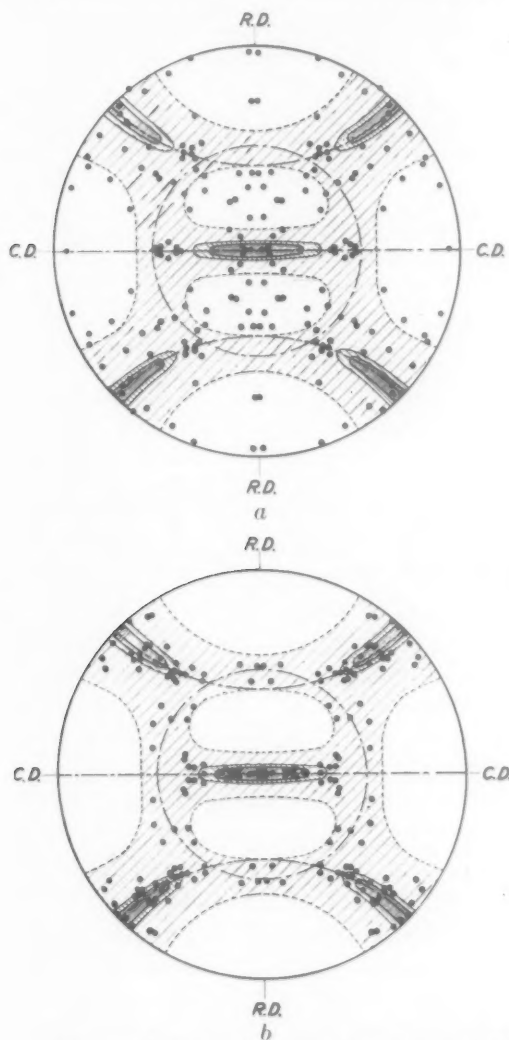


FIG. 7.—INITIAL (a) AND MEAN FINAL (b) CUBE POLES OF 19 CRYSTALS OF TABLE I SUPERIMPOSED ON POLYCRYSTALLINE POLE FIGURE (FIG. 6).

crystalline pole figure have moved into the shaded regions.

CONCLUSIONS AND DISCUSSION

When a single crystal is rolled in a manner simulating the deformation of a grain in an aggregate, it rotates into the vicinity of one or more positions having indices for

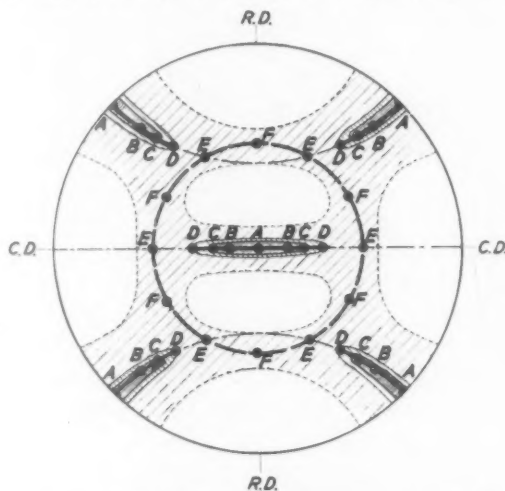


FIG. 8.—STEREOGRAPHIC PROJECTION OF END ORIENTATIONS IN ROLLED SINGLE CRYSTALS OF IRON SUPERIMPOSED ON POLYCRYSTALLINE ROLLING TEXTURE.

Filled circles are $\{100\}$ poles of orientations A to F. Heavy full line is first continuous set containing A to D; heavy dashed circle is second continuous set, containing E and F.

These are plotted in Fig. 8, where three cube poles are plotted for each orientation. These are lettered to correspond to the list above, and are superimposed on the polycrystalline $\{100\}$ pole figure. When there are two symmetrical orientations with similar indices, both are plotted. The orientations are illustrated by a model in Fig. 9, in which the unit cells of the lattice are represented by appropriately tilted cubes arranged symmetrically on a board representing the rolling plane.

It is evident from Figs. 8 or 9 that positions A, B, C and D form a sequence, and it is an important fact that crystals rotating into a position in this sequence spread only 2° or 3° each way about the normal direction as an axis, but spread 7° or 8° each way about the rolling direction as an axis (cf. Fig. 1, for example). These orientation ranges exist within the small area about a millimeter in diameter struck by the X-ray

beam; in addition, there is a continuous variation in orientation across the width of the specimen. This macroscopic variation has been found (by the optical method) also

having (111) in the rolling plane—types *E* and *F*—show large spreads about the *normal* direction as an axis. For example, crystal 12-2, initially within 10° of a (111)

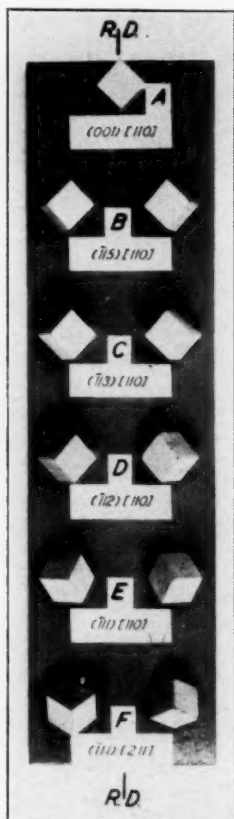


FIG. 9.—MODEL ILLUSTRATING END POSITIONS OF UNIT CELLS IN ROLLED SINGLE CRYSTALS OF IRON.

Reader is looking at rolling plane, with rolling direction vertical, *R.D.* Position *A* and the pairs of symmetrical positions *B*, *C* and *D* form one continuous set, and the symmetrical pairs *E* and *F* another.

to consist almost entirely of a variation about the rolling direction as an axis, often as much as 15° each way from the mean. The angular distance between any two adjacent members of the series *A* to *D* is less than the total spread observed in the usual crystal. It seems best, therefore, to consider positions *A* to *D* as members of a *continuous set* that includes all orientations having $\{110\}$ in the rolling direction and $\{001\}$ between 0° and 45° or 55° from the rolling plane. On the other hand, crystals

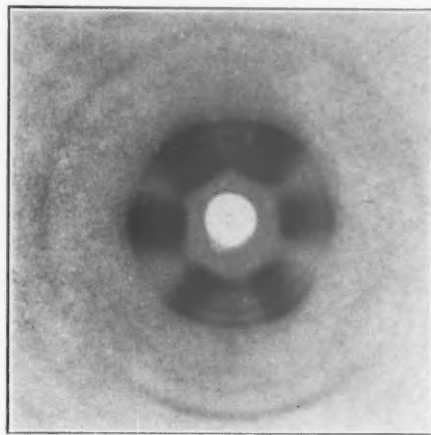


FIG. 10.—LAUE PHOTOGRAPH OF CRYSTAL 12-2 AFTER 97 PER CENT REDUCTION.

Rolling direction vertical; rolling plane in plane of paper.

$[211]$ position rotated into that position with the large azimuthal spread shown in the X-ray photograph of Fig. 10 (indicating possible weak (111) $\{110\}$ and intermediate textures). Since an azimuthal spread of $\pm 15^\circ$ merges types *E* and *F*, we may consider them as members of a second continuous set of orientations that includes all orientations having (111) in the rolling plane. The first set is shown in Fig. 8 by the heavy full lines, and the second set by the heavy dashed circle. Preference toward exact positions within the sets may exist for single crystals, but its actual demonstration would require high reductions and small spreads—two conditions that are difficult or impossible to achieve simultaneously. Such preference cannot be expected in a polycrystalline aggregate because of the mutual interaction of the grains, which causes heterogeneity in the flow.¹⁰

In addition to establishing the end orientations discussed above, the experiments indicate that the polycrystalline pole figure is the sum of these end positions (Figs. 7*b* and 8). An individual grain of an aggregate

may reach one or several of these end positions, depending upon its orientation and its interaction with neighboring grains.

Regarding the theory of the rolling texture, there may be some significance in Wever's point of view¹ that the polycrystalline texture is the superposition of tension and compression textures. The first set of end positions, which corresponds to the tension texture, is composed of grains whose chief spread is around the tension axis, just like the grains in a drawn wire,⁹ while the second set, corresponding to the compression texture, has large spreads around the compression axis, like the [111] component of the true compression texture.⁸ Yet, as has already been pointed out by Gensamer and Mehl,⁵ the theory fails to explain why the complete tension texture does not appear: there is no material with [110] in the rolling direction having (001) at an angle to the rolling plane between 55° and 90°. Furthermore, one orientation only of the minor constituent of the compression texture⁸ is present; namely, (001) [110]. In fact, there are only two end positions consistent with the requirements of both tension and compression; namely, *A* and *E*.

The three "ideal" orientations of Kurdjumow and Sachs, (001) [110], (112) [110] and (111) [$\bar{1}\bar{1}2$], have been found to be end orientations of single crystals, but the rest of the pole figure is not to be explained as a spread about these three orientations alone, for the present study has shown the existence of a number of other end positions and has indicated that there are, in fact, two continuous sets.

No theory has been worked out to date that will predict these end positions of the rolling texture on rigorous grounds. The complexity of the slip mechanism in iron makes Taylor's method^{14,15} extremely laborious, for if there are 48 slip systems there will be 1,712,304 combinations of five from which the correct combination must be chosen for each crystal orientation, and

it is our belief that no theory can succeed in predicting rotations of individual grains, because of the interaction of neighboring grains.¹⁰

SUMMARY

Twenty-six single crystals of decarburized mild steel were rolled by a technique simulating the deformation of grains of an aggregate, and the contribution of each to the texture of the aggregate was determined. Depending on the initial orientation of both the normal and rolling directions, some crystals maintained or rotated into a reasonably sharp single orientation during deformation; others rotated into two or more such orientations, and some fragmented and approached the entire polycrystalline texture. The polycrystalline texture is to be understood as the sum of the end positions approached by these, which consist of two continuous sets—one set with the [110] direction in the rolling direction and with the (001) plane at any angle up to 45° or 55° from the rolling plane, this set containing the positions (001) [110], ($\bar{1}15$) [110], ($\bar{1}13$) [110] and (112) [110]; and a second set with (111) in the rolling plane and with all positions of the rolling direction. The spread in orientation of a crystal that rotates into the first set is chiefly a spread about the rolling direction as an axis; while the spread for the second set is chiefly about the normal to the rolling plane.

ACKNOWLEDGMENT

We are pleased to acknowledge the assistance of Mr. G. V. Smith in the preparation and rolling of crystals.

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DISCUSSION

(George Sachs presiding)

C. D. COXE,* Bridgeport, Conn.—Has Dr. Barrett attempted to correlate his pole figures with the tendency of cold-rolled steel strip to form "ears" or scallops when drawn into a cup?

W. M. SAUNDERS, JR., Providence, R. I.—Since the subject of ears on deep-drawn cups has been brought up, and the correlation of ears with orientations, the results of some unpublished work¹⁶ may be of interest. Using low-carbon cold-rolled strip produced under commercial conditions, no data could be obtained by X-rays that would show the orientations

existing in the well-annealed strip for deep-drawn cups. Attempts to correlate the type of ears, either 45°, or the more common 90° ears, by pole figures, were entirely unsuccessful. As others have found, the degree of cold-work is not sufficient in this kind of material to give data for pole figures. It is possible to predict, however, by using the magnetic balance, what the type of ears will be, or whether low-carbon strip will produce ears. Again, there is uncertainty regarding the orientation of the grains but a specific type of torque curve obtained by the magnetic balance indicates without fail what the ears will be, and qualitatively their height. Low-carbon steel strip, therefore, can be tested before use, to find out whether it will ear or not, and if it does whether 45° or 90° ears will result, and their approximate height. It was found, too, that normalizing of the cold-rolled strip gave freedom from ears, and a considerable amount of cold-rolling, at least 30 per cent cold reduction after normalizing, retained in the strip ear-free properties.

C. S. BARRETT AND L. H. LEVENSON (authors' reply).—We are obliged to Mr. Saunders for his discussion of magnetic torque measurements and their correlation with earing. It is our understanding that present-day deep-drawing sheet is remarkably isotropic, as a rule, and the sensitive magnetic test is probably one of the few ways of showing the slight directionality that is left. It is generally accepted, we believe, that the magnetic tests are far more sensitive than X-ray pictures for showing traces of preferred orientations.

Replying to Mr. Coxé, we have made no cups from the small single crystals used in this study, but undoubtedly many of the crystals that rolled into highly preferred orientations would yield pronounced ears if they were drawn into cups.

* Research Division, Remington Arms Co.

¹⁶ W. M. Saunders, Jr.: Thesis for Sc. D. at Massachusetts Institute of Technology (1939).

Mechanism of Martensite Formation

BY ALDEN B. GRENINGER,* MEMBER, AND ALEXANDER R. TROIANO,† JUNIOR MEMBER A.I.M.E.

(New York Meeting, February 1941)

SUMMARY‡

THE crystallographic mechanism for the austenite-to-martensite transformation has been deduced from the results of the following new experimental determinations: (1) the accurate evaluation of the lattice relationship between austenite and individual crystals of martensite—and thus the relationship between the martensite lattice and the martensite plate, and (2) the measurement and analysis of the change in positions that a volume of austenite undergoes when it transforms into a crystal of martensite. For the latter study, a new tool was developed, the stereographic analysis of shear.

Lattice relationship.—Thirty-five separate 50-gram melts of an alloy containing about 22 per cent nickel and 0.8 per cent carbon were prepared in a high-vacuum furnace. This alloy is all-austenite at room temperature; grain size was about 1 cm. Specimens of the alloy were cooled to about -70°C . to form a few martensite crystals, and suitable specimens were ground and polished on a surface parallel to a single martensite plate, exposing the martensite crystal for an area of 1 mm. or more. Four martensite crystals from four

different ingots were prepared in this manner; the largest crystal of this group is illustrated in Fig. 1. Back-reflection Laue patterns were obtained from martensite

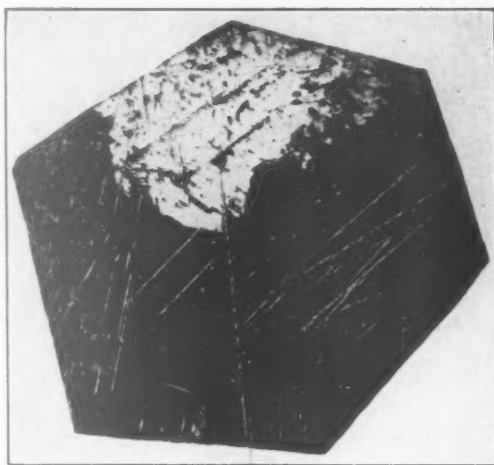


FIG. 1.—MARTENSITE CRYSTAL IN NICKEL STEEL. $\times 6$.

White area is a single crystal of martensite. Etched with Nital. Details of specimen preparation are given in the paper.

crystals (and the matrix austenite) both before and after tempering. The locations of the basal-plane pole of martensite was checked by means of oscillating crystal X-ray patterns.

All four crystals studied yielded the same solution ($\pm 0.5^{\circ}$), and these relationships are expressed in gnomonic projection in Fig. 3.* The narrow dark-etching bands often visible in martensite "needles" were found to be parallel to $\{112\}$ and thus are undoubtedly twin bands in the martensite crystal.

* Figs. 1 through 11 appear in the complete paper. Only Figs. 1, 3 and 6 are shown here.

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‡ The entire manuscript, consisting of 38 pages of text and 11 figures, is available in the form of microfilm (images 1 inch high on standard 35-mm. motion picture film) or photoprints (6 \times 8 inches in size) readable with unaided eyes. For paper, write American Documentation Institute, Offices of Science Service, 2101 Constitution Avenue, Washington, D. C., asking for Document No. 1511 and remitting 69 cents for microfilm or \$5.10 for photoprint copy.

On the Equilibrium Solidification of Solid Solutions

BY MORRIS COHEN,* MEMBER A.I.M.E., AND WILLIAM P. KIMBALL†

(Cleveland Meeting, October 1940)

ABSTRACT‡

THIS paper deals with the calculation of the composition of the infinitesimal trace of alloy that transfers from the liquid to the solid state at each temperature

during the cooling. A general expression for the composition (δ) of the liquid-to-solid transfer at each temperature has been derived:

$$\delta = \frac{Z_L x_L (x_L - P) + Z_S x_S (P - x_S)}{Z_L (x_L - P) + Z_S (P - x_S)} \quad [1]$$

where Z_L and Z_S are the slopes of the liquidus and solidus lines at the given temperature, x_L and x_S are the compositions of the stable liquid and solid phases at the same temperature, and P is the composition of the alloy under consideration. The δ equation is valid for the process of equilibrium heating as well as cooling, and may be applied to vapor-to-liquid, vapor-to-solid, liquid-to-liquid, and solid-to-solid transfers if the corresponding equilibrium diagrams are known.

The δ -versus-temperature curves for two alloys P_1 and P_2 are shown in Fig. 1. In each case, the liquid-to-solid transfer has the same composition as the stable solid phase only at the temperature of the beginning of solidification, and has the same composition as the stable liquid phase only at the temperature of the completion of solidification. At each intermediate temperature, the composition of the liquid-to-solid transfer differs by a finite amount from those of the two coexisting phases. Therefore, during equilibrium cooling, the transfers must merge into the solid phase from the liquid without forming a transition phase; otherwise the condition of equilibrium would be violated. At any given temperature during solidification, the composition of the liquid-to-solid

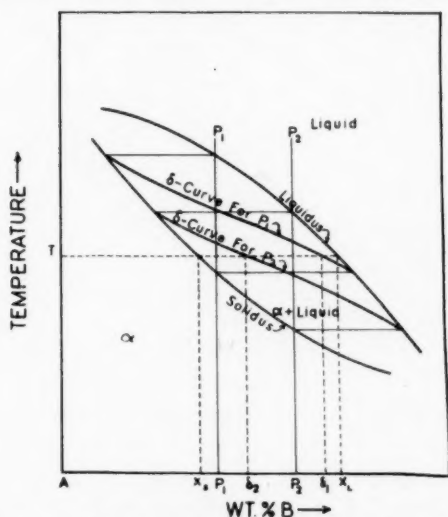


FIG. 1.—GENERAL SOLID SOLUTION DIAGRAM SHOWING δ CURVES FOR ALLOYS P_1 AND P_2 .

during the equilibrium solidification of a binary solid solution, and which thereby enables the compositions of the coexisting liquid and solid phases to follow along the liquidus and solidus lines respectively

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‡ Manuscript received at the office of the Institute June 27, 1940. The entire manuscript has been submitted to the American Documentation Institute, 2101 Constitution Avenue, Washington, D. C., for issuance in the form of microfilm or photoprint. The derivation of the equations and their physical significance are discussed in detail in the paper. For entire paper, write to the American Documentation Institute, ordering Document 1440 and remitting thirty-five cents for microfilm (read enlarged on machines widely available) or one dollar and eighty cents (\$1.80) for photoprint (readable without optical aid). This abstract was issued as T.P. 1256 in METALS TECHNOLOGY, December 1940.

transfer is richer in per cent B, the lower the per cent B in the alloy as a whole.

In the general case, the values of Z_L , Z_S , x_L and x_S which appear in the δ equation are determined graphically from the equilibrium diagram. However, if the equations of the liquidus and solidus lines are known, δ may be expressed explicitly as a function of the temperature. For example, if the liquidus and solidus lines are straight over the solidification range and intersect on the temperature axis at the melting point T_A of component A, the δ -versus-temperature curve becomes a parabola:

$$\delta = \frac{(T_A - T)^2}{Pm_Lm_S} \quad [2]$$

where m_L and m_S are the constant slopes of the liquidus and solidus lines. In such a straight-line system, it turns out that the weight of component B contained in each liquid-to-solid transfer is independent of the temperature and the composition of the alloy, even though equation 2 shows

liquid-to-solid transfers must be accomplished merely by variations in the weight of component A contained in the transfers.

Calculated δ curves for five iron-carbon

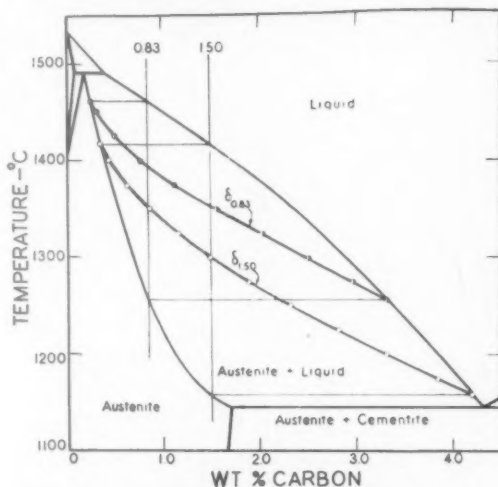


FIG. 2.—PORTION OF IRON-CARBON DIAGRAM SHOWING δ CURVES FOR ALLOYS CONTAINING 0.83 PER CENT AND 1.50 PER CENT CARBON.

alloys are shown in Figs. 2 and 3. The curves in Fig. 3 have interesting discon-

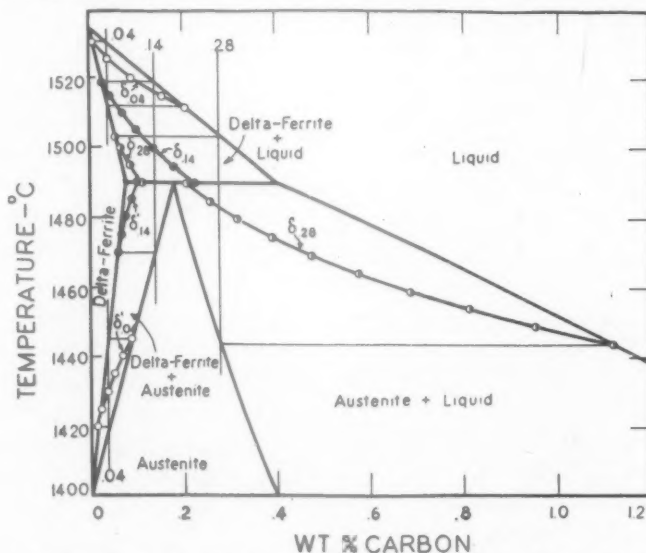


FIG. 3.—PORTION OF IRON-CARBON DIAGRAM SHOWING δ CURVES FOR ALLOYS CONTAINING 0.04 PER CENT, 0.14 PER CENT AND 0.28 PER CENT CARBON.

The δ' curves give compositions of solid-to-solid transfers corresponding to conversion of delta ferrite into austenite during equilibrium cooling.

that the percentage of B in the transfer depends upon both these factors. Accordingly, variations in the composition of the

tinuities because of the peritectic reaction that interrupts the normal course of solidification.

Flow of Solid Metals from the Standpoint of Chemical-rate Theory

BY WALTER KAUFMANN*

(New York Meeting, February 1941)

ABSTRACT†

EYRING's general theory of shear rates as a function of the properties of molecular units of flow is outlined and applied to the creep of metals. This theory regards the unit molecular processes involved in the flow of matter as typical chemical reactions requiring an energy of activation in order to proceed. The externally applied stresses are assumed to influence the rate of flow solely by lowering the activation energy for flow in one direction and raising that for flow in the other, owing to the work that is done by or against the external forces in going from the normal to the activated state. The rates of flow in the two directions are then no longer equal and there is a net, macroscopically observable flow in one direction. This is understood to be the physical basis for the well-known exponential dependence of the creep rate on the stress. The amount by which the activation energy is raised and lowered by a given external stress is directly related to the molecular dimensions of the unit of

flow, so that some insight into these can be found from the behavior of the strain rate with changing stress.

When Eyring's equation is applied to the flow of ordinary liquids, such as water or benzene, it has been found from the values of the constants required to fit the observed data that the unit molecular process here involves the passage of single molecules by one another. In metallic creep, on the other hand, the unit molecular process is shown probably to involve the shear of rather large blocks of material (100 to 1000 or more atoms on a side). This agrees with present ideas of crystal flow by means of dislocations* such as have been presented by Taylor, Orowan, and Polanyi, as opposed to flow by a mechanism related to that taking place in atomic diffusion. The dimensions of the dislocations are found to depend markedly on the temperature.

The questions of why some metals are so much softer than others, the effects of impurities on hardness, the softness of single crystals, and the role of self-diffusion in creep are considered in the light of the theory and it is shown how answers to these questions (and others similar) might be obtained by use of the theory.

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Surface Finish and Structure

By JOHN WULFF,* MEMBER A.I.M.E.

(Cleveland Meeting, October 1940)

IN a previous paper Burwell and Wulff¹ have shown by electron diffraction studies that allotropic transformations can be induced in 18-8 stainless steel by polishing to a depth of about 5×10^{-5} cm. The development of a successful etching technique, which removes accountable amounts of metal from the surface without pitting and without changing the root-mean-square profile as measured with an Abbot profilometer, led to the application of the whole technique and material to an investigation of various mechanical methods of surface preparation, such as grinding, lapping, superfinishing and cold-rolling.

Ideally suited to such a study is 18-8 of low carbon and nitrogen content. The material can be heat-treated to produce a coarse-grained single-phase structure. On cold deformation there occurs not only a reduction in grain size but, at regions of maximum stress, a change of face-centered material to body-centered material, provided the metal is worked below about 200°C. When worked between 200° and 415°C., diffraction studies evidence a reduction in grain size without the appearance of any new body-centered ferrite. Ferrite, which can be referred also to strains induced by carbide precipitation, is evident when the material is worked at temperatures between 415° and 800°C. Stainless steel is advantageous because the usual surface-finishing operations do not readily oxidize it to any appreciable depth. In

order to produce detectable oxide films on the surface of austenitic 18-8 in a time equivalent to that required to produce, for example, a fine ground finish on $\frac{1}{2}$ sq. in., the sample must be held in a furnace or oxygen stream above 600°C. By using longer heating times, it is possible to achieve measurable oxide films on samples whose surface temperatures exceed only about 250°C.

EXPERIMENTAL PROCEDURE

The apparatus, material, and technique described in the previous paper¹ were employed in this investigation. Samples of 18-8, 1 by 1 cm. by 4 mm., were carefully annealed in the austenitic range to produce a coarse-grained structure. They were then quenched and pickled to remove scale. On a lapping machine of the Graton² type, both sides of each sample were polished to a flatness of $\frac{1}{16}$ a wave length of sodium D light. Thereafter they were electrolytically etched to remove at least 1×10^{-3} cm. of the surface, a depth that is well below that of any deformations induced by surface preparation. Samples of this material, carefully mounted in steel holders, were then sent to various industrial organizations known for special finishing techniques. In the instrument shops at the Massachusetts Institute of Technology check samples were finished by the same methods, as far as they were available. Abbot profilometer³ readings were made on all the samples, which were then carefully degreased in double distilled benzine and alcohol, dried in a hot-filtered air blast, and kept in a desiccator. Suc-

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¹ References are at the end of the paper.

cessive electron diffraction pictures were obtained from these surfaces from the as-finished to the deeply etched state. Material was removed from the surfaces in amounts equivalent to from 30 to 100 Å. in thickness, the total amount removed extending to depths of 3 mm. Periodical profilometer measurements indicated that the technique did not alter the root-mean-square profile of the surface. Nevertheless, microscopic examinations by dark and light field illumination definitely illustrated the fact that etching had changed the true profile. Later, this change was found not to interfere with the magnitude of effects described in this paper.

It is necessary to point out that the dry-ground samples were obtained with a two-motion grinder operating at high speeds and pressures and giving unidirectional scratches. The wet grinding was accomplished at essentially the same speeds and pressures but with multimotion grinders. The honing motion possesses fewer degrees of freedom than do the other methods, except the dry-grinding method. Grinding, honing, sanding and superfinishing were accomplished with a fixed abrasive, whereas for lapping and metallographic polishing the abrasive was applied as a suspension to the cloth or metal lap. Even with these processes, it is very probable that the removal of surface metal is accomplished efficiently only by the part of the abrasive that is charged into the lap. This condition is in contrast to that of finishing glass, where rolling, loose abrasive probably accounts for surface removal.

The results of the study are schematically described in Fig. 1. The actual patterns obtained are similar to those previously published.¹ It should be emphasized that each sample used gave a profilometer reading of from 1.4 microinch to 2.8 microinches and that only the dry-ground samples gave initial diffraction patterns that were other than two diffuse rings. When grinding was accomplished dry with a vitreous bonded

wheel, the pattern was that of an oxide; when accomplished with a resinous bonded wheel, the pattern consisted of a superposition of oxide pattern and rings similar to those obtained from resinous varnish films. When the electron beam was reflected from ground surfaces parallel to the grinding marks on fresh surfaces, two diffuse rings were obtained; but when reflected perpendicular to the scratches, the diffuse rings were less intense and permitted a study of a weak pattern of oxide. After 100 Å. was removed from the dry-ground surface the oxide rings became fainter and after about 1000 Å. could not be detected. More than 2000 to 3000 Å. had to be removed, however, before this type of surface gave a pattern whose structure could be easily identified. Nevertheless, the distribution of intensity of the diffuse pattern strongly suggested a preferred orientation. After 10 to 50 Å. of surface material had been etched, the diffuse patterns of the unground surface finishes readily gave way to rings of identifiable crystalline material, regardless of which way the electron beam impinged on the surface.

The persistence of diffuse rings to a depth of 3000 Å. on the ground surface led to the following experiments: Upon a thin, wet Bakelite varnish coating on glass, the same floated alumina commonly used on the last metallographic wheel was dusted in the dry state and the whole was allowed to dry. A 2-microinch ground sample and a superfinished sample were then lightly rubbed on this surface by hand until both gave profilometer readings of 5.8 microinches. The electron diffraction picture of the superfinished surface immediately exhibited a crystalline pattern of ferrite, whereas the ground surface still gave a diffuse pattern. Further abrasion of the ground sample—which did not change the root-mean-square profile appreciably but which, to judge from the thickness of the ferrite layer uncovered, undoubtedly removed from its surface material equivalent

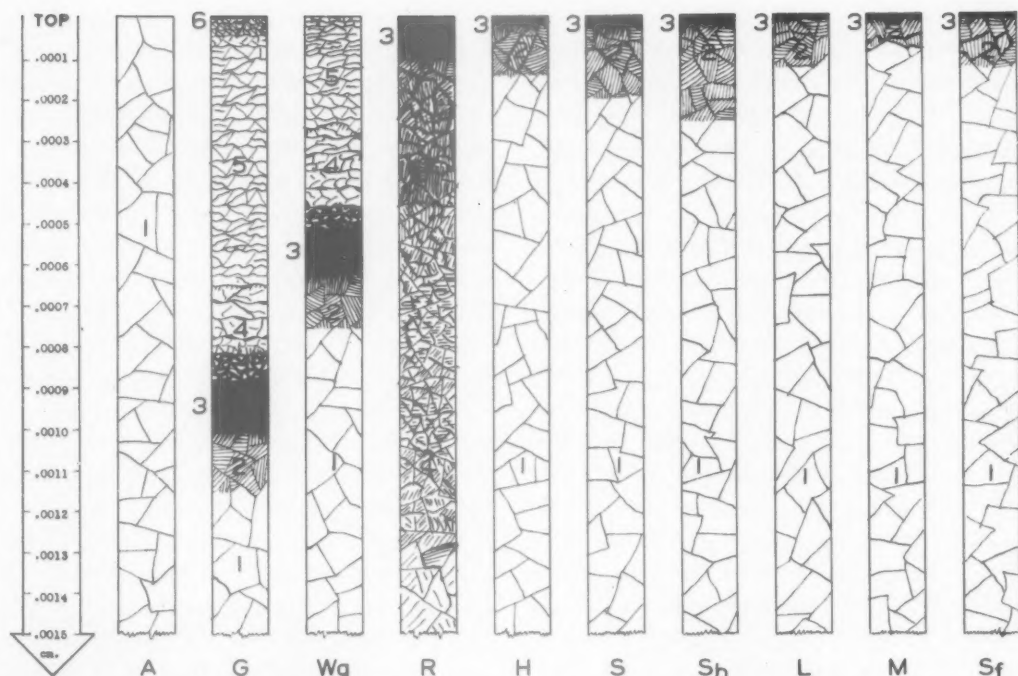


FIG. 1.—SCHEMATIC REPRESENTATION OF ELECTRON DIFFRACTION STUDIES OF SURFACES FINISHED TO APPROXIMATELY THE SAME AVERAGE SMOOTHNESS BY DIFFERENT TECHNIQUES.

Patterns were obtained of the surfaces as finished and after successive electrolytic etchings with a 10 per cent oxalic solution. The relative percentage of austenite and ferrite present in the fields of the diagram were estimated from the relative intensity of the separate diffraction patterns. An accuracy not greater than 10 per cent is to be expected in such determinations, yet this order of magnitude is sufficient to illustrate the comparison between the different processes. In the cold-rolled specimens the degree of uncertainty is much smaller, for all measurements could be checked by magnetic-moment studies.

A, coarse-grained austenitic structure produced by annealing and determined by electron diffraction patterns after deep electrolytic etching to remove effects of lapping; reading on Abbot profilometer, 1.8 microinches.

G, finely ground surface; 2.2 microinches; grinding scratches in one direction.

W_g, wet ground, multimotion technique, 2.1 microinches.

R, same material as *A* reduced cold in rolls 50 per cent, 2.6 microinches.

H, honed, 2.2 microinches.

S, sanded, scratches put on by belts moving in one direction 2.8 microinches.

S_h, sanded by hand. Specimens finished entirely by hand on fine papers. Pressure greater but speed less than *S* 2.6 microinches.

L, mechanically lapped; finish accomplished with multimotion machine of the Graton type using series of different metallic laps, 1.4 microinches.

M, metallographic polish, 1.4 microinches.

S_f, Chrysler Superfinish, 1.4 microinches.

1, annealed; coarse-grained austenite, face-centered.

2, coarse-grained austenite plus cold-worked ferrite (body-centered).

3, all cold-worked ferrite.

4, cold-worked ferrite plus deformed austenite.

5, deformed austenite.

6, distinguishable oxide.

7, severely deformed grains with oxide and abrasive binder contaminations.

8, cold-worked ferrite cannot be distinguished by electron diffraction methods at greater depths than about 0.03 cm. yet magnetic-moment measurements indicate small percentages present throughout the material below this depth.

to 6×10^{-4} cm. in depth—gave definite ferrite patterns. Each diffraction picture of the ground surfaces showed that until the basic coarse-grained austenitic layer was uncovered, the rings of identifiable crystalline material were broader and more diffuse than those patterns of more gently finished surfaces, such as are produced by lapping, superfinishing and metallographic polishing. Only cold-rolling gave patterns of broadness similar to those of ground surfaces.

The surface of the cold-rolled material gave a profilometer reading of 2.6 micro-inches. Like metallographically polished surfaces, this material initially gave a two-diffuse-ring-diffraction pattern with some evidence of preferred orientation. Only after etching 10 to 50 Å. of the surface was it possible to uncover a definite crystalline pattern, albeit the rings persisted as broad rings to depths greater than 1×10^{-4} cm.

DISCUSSION AND CONCLUSIONS

In considering the results of this work, it is well to keep in mind that in the grinding process the abrasive travels at high speed and high pressure in contact with the work, whereas in rolling or burnishing the finishing is accomplished at slow speed and high pressure. In lapping, mechanical as well as manual sanding, usual honing operations, superfinishing, and metallographic polishing, the abrasive travels at a relatively slow speed, and a minimum pressure is exerted.

Of greatest interest is the observation that to a depth of 6.3×10^{-4} cm. of the dry-ground surface, occurs, essentially, fine-grained but severely distorted austenite. For this material to have remained face-centered means that during deformation the lower boundary must have been above about 200°C. By the use of the classical theory of heat flow, by making reasonable assumptions for contact area, energy input, and coefficient of friction, and by employing simplified boundary conditions, it is possible to calculate that the surface temper-

ature of the top layer of atoms of the material will be between about 700°C. and the melting point of the metal. Although such flash temperatures may exist, they will never reach depths of 6.3×10^{-4} cm. before, or at the same time as, the effects of mechanical deformation. In the grinding studied, the work moves to another point of contact before the thermal flash reaches the point and depth considered. Any superposition of the effects of thermal flashes at the depth considered is not large enough to give an average temperature of greater than 200°C. Auxiliary experiments of rolling this material at different temperatures and achieving ferritic surfaces only below about 200°C. led to the belief that the presence of deformed austenite can be attributed to heat engendered during the severe and rapid rate of plastic deformation encountered in the grinding process. This statement, however, is not intended to rule out the possibility of flash temperatures as high as those calculated and suggested by Bowden.⁴ Some basis for his opinion is found in the presence of an oxide film 100 Å. thick on the top surface. Such a film can be produced on 18-8 alloy only by holding the metal at temperatures above about 600°C. for a time equivalent to that necessary to produce a fine ground surface. For a sample 1 cm. by 1 cm. by 4 mm., this time is less than a minute. The wet-ground surface does not give a discernible surface oxide pattern, although the latter may be found for plain-carbon-steel surfaces prepared in this way.

All of the other finished surfaces show only the effects of surface deformation below 200°C. Although plastic deformation is evident in every one, in none is the working speed such as to give surface flash temperatures greater than 200°C., nor is there any evidence of temperatures from plastic deformation greater than 200°C.

Since Germer,⁵ Kirchner⁶ and Burwell⁷ have ably pointed out that the reflection electron diffraction method is not a unique

way of determining the presence on metal of amorphous films resulting from polishing techniques, this paper does not propose to explain the double diffuse ring pattern obtained for all the surfaces on the amorphous film basis. More recent remarks of Bragg⁸ and transmission electron diffraction work of Cochrane^{9,10} imply further that if an amorphous metallic state of metals occurs, it is extremely short lived. Nevertheless, the persistence on our finely ground samples of such diffuse patterns to depths of 3×10^{-5} cm. certainly suggests that the metal to this depth is severely distorted. This distortion, coupled with the fact that in this layer it is common to find entrapped "muck" originating from resinous bond wheels and entrapped abrasive originating from vitreous bond wheels when used on materials such as 18-8, suggests from a corrosion and wear standpoint the necessity for the removal of the top ground surface by chemical or physical means gentler than that of high-speed grinding.

It is not the intention of the present paper to imply that these results or conclusions apply to all materials. It may be pointed out, however, that in auxiliary experiments, beta brass and bronze, Hadfield's manganese steel, and plain carbon steels exhibit deformation effects to depths of the same order of magnitude as those recorded for 18-8 when they are finished by the same mechanical means and to the same degree of fineness. The results are not so easily obtained nor so readily interpretable as are electron diffraction pictures of 18-8. For fine ground samples, however, it is possible to electroplate the finished surface with nickel for protection, make an oblique section, polish and etch this section, and study under high magnification the region beneath the nickel plate. Preliminary results have been obtained in the laboratory at magnifications of from 1000 to 2300 on beta brass, beta bronze, and Hadfield's manganese steel, all of which show definite transition layers below the

nickel plate to depths of about 1×10^{-3} cm. These layers are, wherever resolvable, extremely fine-grained and distorted as compared to the base materials. Adjacent to, and below, this layer in each of these three alloys, multitudinous stringers of martensite are discernible. These extend to further depths of from 1×10^{-4} to 1×10^{-2} cm., with their markings regularly oriented to the direction of grinding. Numerous small cracks are discernible perpendicular to the finished surfaces in the ground beta brass and bronze, but not when the surface has been prepared by lapping or polishing, for under the latter condition neither cracks nor deformed nor transformed material is resolvable by the microscope. To be sure, cracks form more readily on quenched and untempered brass and bronze of the composition used; yet they are often also found on tool and die steels, and more often on steels that have been carburized. The cracks in such cases are usually of a depth of 1×10^{-2} to 1×10^{-3} cm., commensurate with those found in the nonferrous materials just mentioned. Where such cracks extend deeper, they may initiate because of thermal stresses engendered in grinding; yet when retained austenite exists in the steel, even cold deformation, if it is sufficiently severe, may transform residual austenite to martensite and cause miniature cracks.

ACKNOWLEDGMENTS

It is a pleasure to thank the officers of the Chrysler Corporation for financial assistance; Mr. D. A. Wallace, of that Corporation, for personal cooperation, and Messrs. C. L. Sackett and R. D. Feynman for able laboratory assistance.

SUMMARY

To ascertain the depth and nature of the deformation induced by such finishing processes as cold-rolling, dry and wet grinding, lapping, honing, sanding, super-finishing, and metallographic polishing,

electron diffraction pictures were taken of successively etched 18-8 stainless-steel surfaces. For surfaces of approximately the same root-mean-square profile, the pressure was found to influence the depth of deformation, the speed of work or abrasive, the temperature of the deformation, and thus the nature of the transformation. Experimental results indicate that during fine dry grinding the temperature of the point of contact may be higher than 600°C. and a layer of metal 6.3×10^{-4} cm. directly below this above 200°C. In material that has been cold-rolled, there is no indication of temperature effects that exceed

200°C. In surfaces that have undergone superfinishing, lapping, and metallographic polishing, the depths of deformation do not exceed 1.5×10^{-5} cm., and discernible temperature effects do not exceed 200°C.

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Influence of Austenite Grain Size upon Isothermal Transformation Behavior of S.A.E. 4140 Steel

BY E. S. DAVENPORT,* MEMBER A.I.M.E., R. A. GRANGE* AND R. J. HAFSTEN*

(New York Meeting, February 1941)

THE influence of austenite grain size upon the hardenability of steel is now fairly well understood; for a given austenite, increasing the grain size increases the depth of hardening, and, since the latter is related to the fundamental transformation behavior of austenite, it follows that austenite decomposition must, in general, be retarded by increasing grain size. To date, very little quantitative information bearing directly on the effect of austenite grain size upon the progress and result of isothermal transformation has been published. Davenport and Bain,¹ and Zimmerman, Aborn and Bain² have shown that the transformation is definitely retarded in hypereutectoid plain carbon steels at temperatures near and above the upper region of rapid transformation (A_r') when the austenite grains are increased in size. More recently, Griffiths, Pfeil and Allen³ investigated the effect of a series of different heating (austenitizing) temperatures upon the progress of isothermal transformation at 1245°F. (675°C.) and 745°F. (395°C.) in a medium carbon, low-alloy steel; while they reported no measurements of the austenite grain size, their results suggest that increase in grain size retards austenite transformation at 1245°F. (675°C.), but has no appreciable effect at 745°F (395°C.).

The present paper deals with the results of a study of the isothermal transformation of austenite in a single commercial alloy

steel in which a fine-grained or a coarse-grained state was induced by appropriate selection of austenitizing temperature. The data are presented in the form of isothermal transformation diagrams, which clearly show that coarsening the grains lessens the rate of transformation of austenite to proeutectoid ferrite and pearlite—that is, at temperature levels above about 1000°F. (540°C.)—but is without significant effect at lower temperatures where the transformation product is bainite or martensite. It is to be presumed that the foregoing statement would be valid, at least in principle, for many other grades of steel; it confirms again that the mechanism of transformation to a pearlitic structure is fundamentally different from that to an acicular structure. A number of related observations were made, which seem to throw some light on the transformation process as it takes place in alloy steels, particularly at temperature levels in the vicinity of 1000°F. (540°C.), where the transition from lamellar to acicular structures occurs. These data are discussed briefly in the belief that they may lead to a clearer understanding of this aspect of the subject.

MATERIAL AND EXPERIMENTAL PROCEDURE

The material investigated was a commercial grade of S.A.E. 4140 steel, the composition of which was as follows: 0.37 per cent C, 0.77 per cent Mn, 0.98 per cent Cr and 0.21 per cent Mo. It was hot-rolled to a 1½-in. round bar and normalized by air-cooling from 1800°F. (980°C.).

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¹ References are at the end of the paper.

Specimens were prepared by cutting disks $\frac{1}{16}$ in. thick from the bar and halving them.

A preliminary study of the grain-

and, finally, quenching to room temperature in brine. Metallographic observations and hardness measurements on such specimens served to locate the Ae_1 and Ae_3

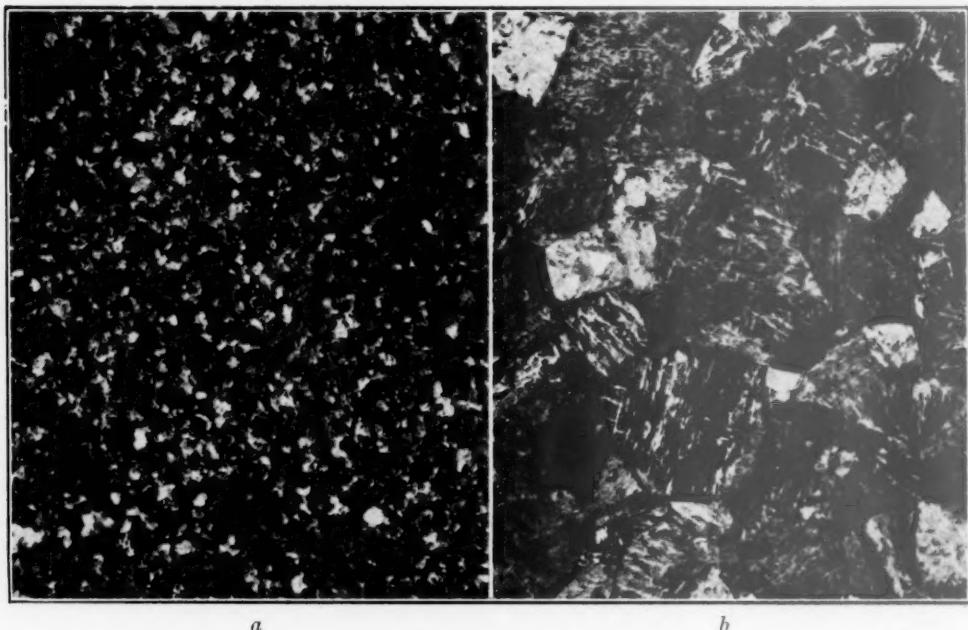


FIG. 1.—AUSTENITE GRAIN SIZE IN FINE-GRAINED AND COARSE-GRAINED STATES SHOWN BY TEMPERED MARTENSITE ETCHED WITH GRAIN-SIZE REAGENT. $\times 100$.
a, austenitized at 1550°F. (845°C.); grain size 7-8 A.S.T.M.
b, austenitized at 2000°F. (1095°C.); grain size 2-3 A.S.T.M.

coarsening characteristics of this steel led to a choice of temperatures of 1550° and 2000°F. (845° and 1095°C.) for producing, respectively, a uniformly fine-grained or a uniformly coarse-grained austenite. At either temperature the specimens were held for 15 min. before quenching into a molten lead-bismuth bath for isothermal transformation. The metallographic method of following the progress of transformation was used; it has been discussed in detail elsewhere,^{4,5,6} therefore need not be fully described here.

The equilibrium transformation temperatures Ae_1 and Ae_3 were determined by quenching a number of specimens from 1550°F. (845°C.) into brine, then holding each of them at a series of different temperatures near the Ae_1 and Ae_3 long enough to attain structural equilibrium

temperatures, the former being the lowest temperature at which a trace of austenite (martensite after the final quench) was produced, and the latter the lowest temperature at which all the ferrite dissolved in the austenite. These determinations were made only on the steel in the fine-grained state; it is assumed that since the Ae_1 and Ae_3 temperatures refer to equilibrium conditions, they are independent of grain size and would therefore be identical for both the fine-grained and coarse-grained states.

INFLUENCE OF AUSTENITIZING TEMPERATURE

The austenitizing treatment consisted of holding for 15 min. at 1550°F. (845°C.) and 2000°F. (1095°C.), respectively, which produced an A.S.T.M. grain size of 7-8 and 2-3, respectively, in the austenite.

The grain size was measured by quenching a specimen from each austenitizing temperature, tempering at 600°F. (315°C.), and then polishing and etching with

cooling rate from those quenched from 1550°F. (845°C.); however, since the cooling was extremely rapid in both cases, any slight difference in the relatively

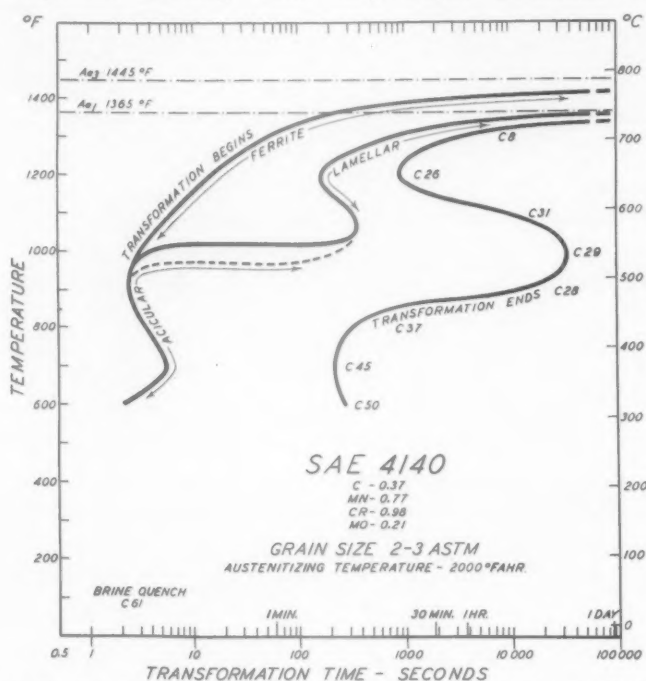


FIG. 2.—ISOTHERMAL TRANSFORMATION DIAGRAM FOR COARSE-GRAINED S.A.E. 4140 STEEL.

“grain-size reagent” (mixed hydrochloric and picric acids in alcohol).⁷ Fig. 1 shows the austenite grain size produced by these two austenitizing treatments.

A holding period of 15 min. at 1550°F. (845°C.) sufficed to dissolve all the carbides; therefore the full carbon and alloy content of the steel was in solution in both the fine-grained and coarse-grained austenites. With the possible exception of a slightly more uniform distribution of the alloying elements due to more rapid diffusion at 2000°F. (1095°C.) than at 1550°F. (845°C.), the austenite was, therefore, chemically identical in the two cases, so that any significant difference in transformation behavior may be attributed to the influence of grain size or to factors associated with it.

Specimens quenched directly from 2000°F. (1095°C.) into the transformation bath may have differed slightly in

short time interval consumed in reaching the temperature of the bath is unimportant in view of the much longer time interval necessary for visible transformation to begin in this steel. That this factor is in fact negligible was confirmed experimentally by interrupting the quench from 2000°F. (1095°C.) long enough at 1550°F. (845°C.) for the specimen to attain this latter temperature before transferring it to the transformation bath; specimens so treated transformed identically, within the limits of the experimental error in the method of estimation used, with those quenched directly from 2000°F. (1095°C.).

ISOTHERMAL TRANSFORMATION DIAGRAMS FOR FINE-GRAINED AND COARSE-GRAINED S.A.E. 4140 STEEL

The isothermal transformation diagram summarizing the results of the study of

the transformation behavior of this S.A.E. 4140 steel in the fine-grained state has already been published (see Fig. 24, p. 865 of ref. 6). The analogous diagram

of ferrite, speckled with what appears to be carbide. A similar behavior has been reported⁶ for S.A.E. 4340 steel transformed isothermally at 900°F. (480°C.).

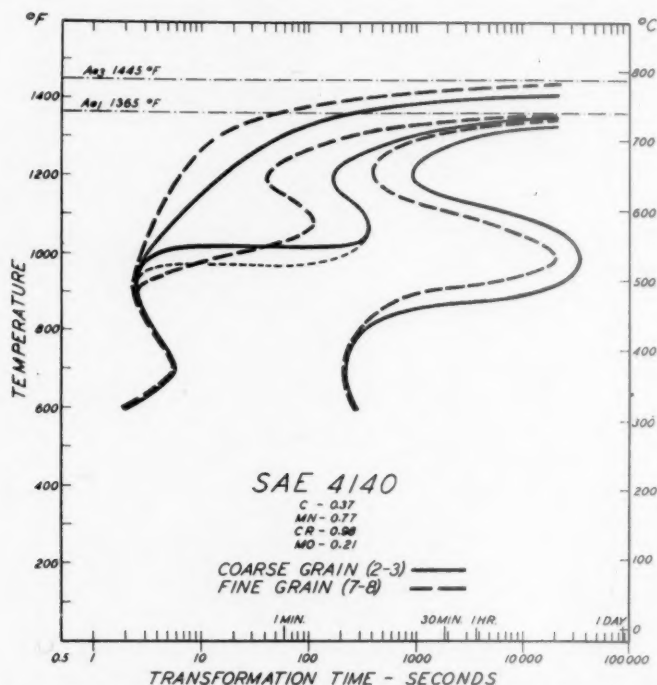


FIG. 3.—ISOTHERMAL TRANSFORMATION DIAGRAMS FOR S.A.E. 4140 STEEL IN FINE-GRAINED AND COARSE-GRAINED STATES.

for the steel in the coarse-grained state is shown in Fig. 2. In this case, transformation below 600°F. (315°C.) was not studied and the diagram is not carried below this temperature. The different curves comprising Fig. 2 are labeled to indicate their significance, and the Rockwell C hardness, after complete transformation at each temperature level investigated, is shown to the right of the curve representing the completion of transformation.

The diagram for coarse-grained S.A.E. 4140 steel (Fig. 2) has a flat "shelf," in the vicinity of 1000°F. (540°C.) in the line representing beginning of transformation to the "ferrite-carbide" product; this is associated with a mode of transformation that involves, in the early stages, the formation of an acicular type

The broken line below the shelf represents the beginning of a second stage in the reaction, following the separation of the speckled ferrite; during this second stage a rapid-etching, acicular type of structure forms. These structures will be discussed more fully later when the metallographic evidence is presented.

The influence of grain size on the position of the beginning and ending curves of the isothermal transformation diagram can best be shown by plotting on a single chart, as in Fig. 3, the curves for both the fine-grained⁶ and the coarse-grained austenite (Fig. 2). This shows that coarsening the grains definitely retarded the transformation at temperatures above about 1050°F. (565°C.) and that, in this region, the effect is simply one of lateral displacement, the shape of the curves being

very similar.* Between 1050°F. (565°C.) and 900°F. (480°C.), the time for beginning of transformation of the coarse-grained austenite gradually approaches that for the fine-grained. Below about 900°F. (480°C.) the curves almost coincide, indicating that grain size has little influence in this range of temperature. In other words, the coarse-grained austenite tends to transform much more slowly than fine-grained only in the upper temperature range where the soft, predominantly lamellar products form; the rate of transformation to bainite is not appreciably affected by grain size.

Simultaneous precipitation of carbide and ferrite in the form of the "speckled, acicular ferrite" appears to occur at a somewhat higher temperature in the coarse-grained steel, this precipitation comprising the initial stage of the two-stage reaction observed in the transformation of coarse-grained austenite at 1000°F. (540°C.).

TABLE 1.—*Influence of Transformation Temperature on Time Required for 50 Per Cent Transformation*

Temperature Level, Deg. F.	Time for 50 Per Cent Transformation of		Ratio t_1/t_2
	Coarse Grain t_1 (Sec.)	Fine Grain t_2 (Sec.)	
1300	1,800	260	6.9
1200	500	150	3.3
1100	2,500	900	2.8
1000	1,200	750	1.6
900	30	30	1
800	35	35	1
700	40	40	1
600	25	25	1

The large effect of grain size in retarding transformation at the higher temperature levels may not be obvious from Fig. 3, because of the logarithmic time scale; it is more clearly shown by Table 1.

* It is to be remembered that when time is plotted on a logarithmic scale a constant lateral displacement of the curves would mean, not a constant difference, but a *constant ratio* of time intervals.

In compiling this table the time interval for 50 per cent transformation at each temperature level was estimated from the experimental data; these "half-transformation" periods constitute a convenient measure of the speed of the transformation. The ratio of this 50 per cent period for coarse-grained to that for fine-grained austenite thus affords a means of evaluating the effect of grain size in retarding the transformation. Such ratios are listed in the last column of Table 1 and show that at 1300°F. (705°C.) the coarse-grained austenite requires about seven times as long for 50 per cent transformation as the fine-grained austenite; as the temperature decreases, the ratio falls off rapidly and at 900°F. (480°C.) becomes unity, showing that in this steel grain size has no effect in retarding transformation at the lower temperatures.

EFFECT OF GRAIN SIZE UPON MICROSTRUCTURE AND HARDNESS

The microstructures resulting from transformation of coarse-grained austenite are more striking and more easily interpreted than those from fine-grained austenite. By increasing the austenite grain size, the "scene" upon which the "action" (structural changes involved in transformation) takes place is, in effect, enlarged, thus making it easier to study the mode of transformation in detail, particularly at borderline temperatures where the character of the product is neither clearly lamellar nor acicular. The photomicrographs of Fig. 4 show the result of partial transformation in fine and coarse-grained austenite at the 1300°F. (705°C.) and 1100°F. (595°C.) temperature levels; they clearly illustrate how the larger grain size makes it easier to study the mode of transformation and the nature of the product. At 1100°F. (595°C.) particularly, the acicular nature of the ferrite-carbide aggregate is much more evident in the coarse-grained structure than in the fine-grained. At each of these

temperatures, however, the fundamental character (lamellar or acicular) of the ferrite-carbide aggregate appears to be

more by the temperature level at which it forms than by any other single factor. Grain size does, however, appear to in-

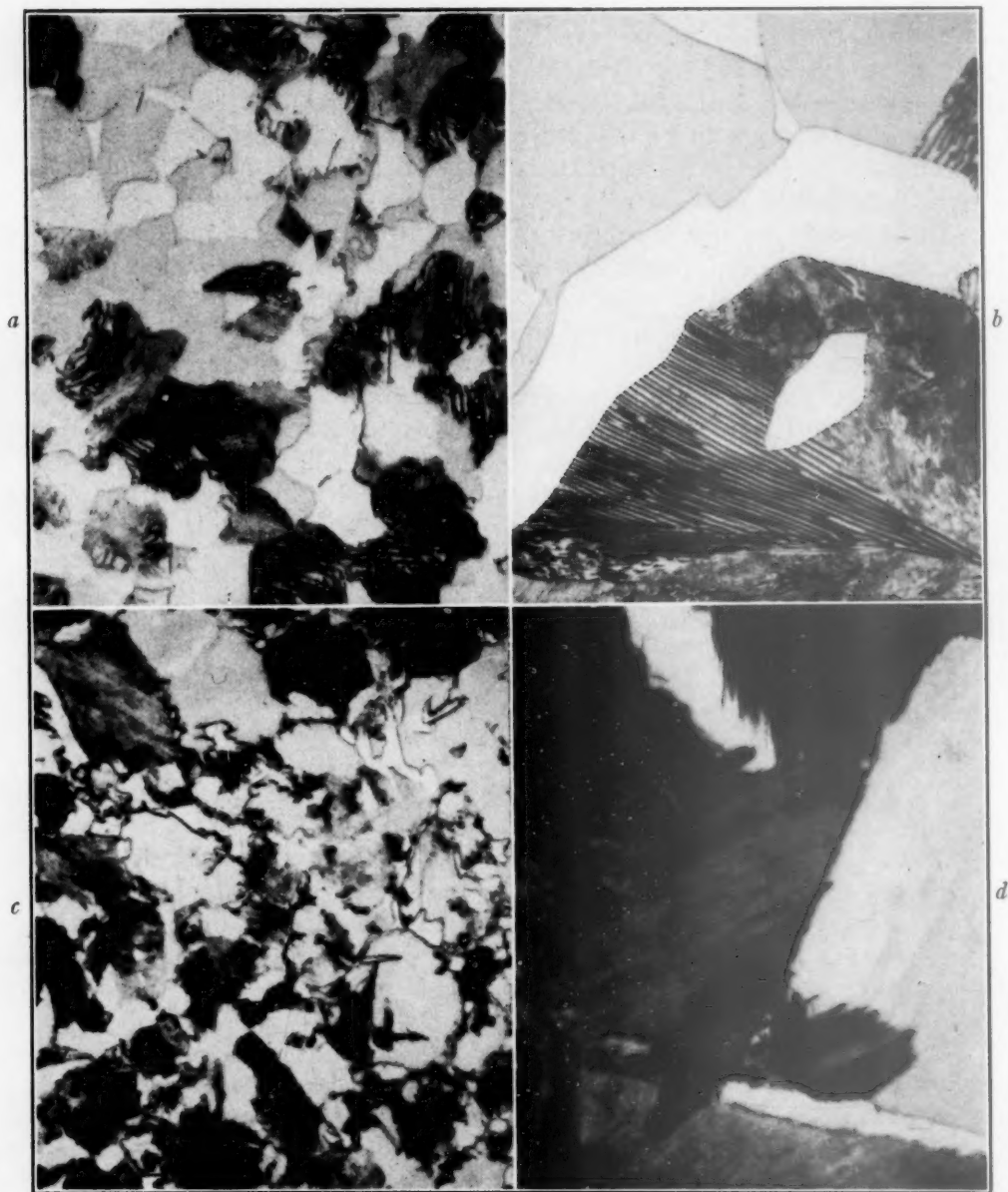


FIG. 4.—PARTIAL TRANSFORMATION IN S.A.E. 4140 STEEL. $\times 1000$.

a, fine grain; 1300°F. (705°C.) level.

b, coarse grain; 1300°F. (705°C.) level.

c, fine grain; 1100°F. (595°C.) level.

d, coarse grain; 1100°F. (595°C.) level.

Etched in Picral + Nital.

essentially unaffected by austenite grain size; this is consistent with the generally accepted view that structure is determined

fluently by the temperature level at which it forms than by any other single factor. Grain size does, however, appear to in-

(650°C.) level where at least twice as much ferrite is rejected from the fine-grained austenite as from the coarse. The photomicrographs of Fig. 5 show this difference

coarse-grained austenite; Fig. 6a represents the initial stage, in which only needles of ferrite, speckled with carbide appear; the rapid-etching, acicular product that

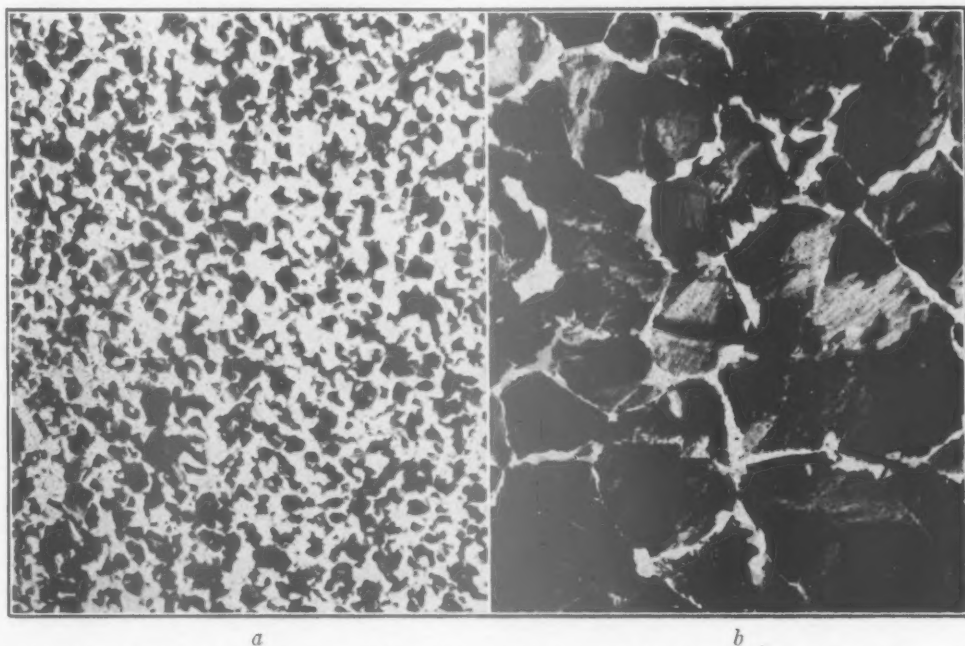


FIG. 5.—INFLUENCE OF AUSTENITE GRAIN SIZE UPON AMOUNT OF FREE FERRITE AFTER COMPLETE TRANSFORMATION AT 1200°F. (650°C.). $\times 200$.

a, fine grain.
b, coarse grain.
 Etched with Nital.

in the amount of ferrite present after complete transformation.

As mentioned earlier, two distinct stages were observed in the transformation of coarse-grained austenite at 1000°F. (540°C.); the first stage is, in many respects, analogous to the separation of the proeutectoid ferrite that occurs in the range from the A_{e_3} down to about 1000°F. (540°C.), but must be considered as somewhat different because of the acicular or Widmanstätten form of the ferrite and the presence of what appears to be carbide in many of these ferrite needles. The same sort of structure has been described by others, notably Davenport⁶ and Jolivet.⁸ The photomicrographs of Fig. 6 show the character of the product resulting from transformation at 1000°F. (540°C.) of

distinguishes the second stage of the reaction makes its appearance in 6b. Figs. 6c and 6d represent complete transformation, the former at a magnification of $\times 1000$ and the latter at $\times 2000$; the speckled appearance of the ferrite needles, even after complete transformation, is particularly evident in 6d. In the case of the fine-grained austenite transforming at 1000°F. (540°C.), the presence of carbide particles in the ferrite needles and the definite separation of the reaction into two stages is not so apparent, although careful examination revealed an occasional speckled ferrite needle. At 900°F. (480°C.) and below, the only apparent difference in the character of transformation product from the fine and coarse-grained austenite

was in the larger size of the bainite needles in the latter.

at corresponding temperature levels reveals that they differed significantly only at

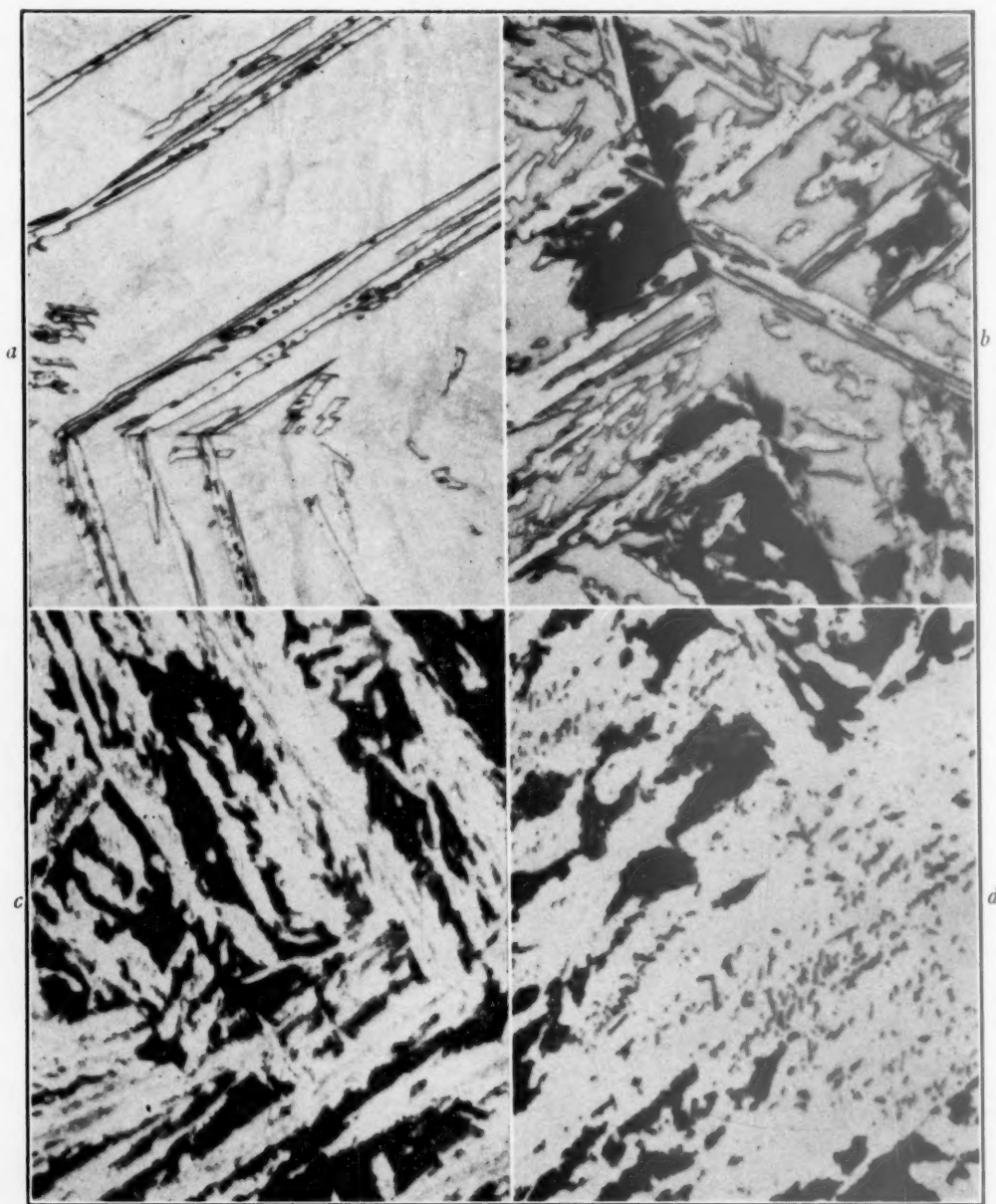


FIG. 6.—DIFFERENT STAGES IN TRANSFORMATION OF COARSE-GRAINED S.A.E. 4140 STEEL AT 1000°F. (540°C.).

a, initial stage, $\times 1000$.

b, second stage, $\times 1000$.

c, transformation complete, $\times 1000$.

d, transformation complete, $\times 2000$.

Etched with Picral + Nital.

Comparison of the hardness of the fine-grained structure with the coarse-grained structure after complete transformation

one temperature level; namely, 1200°F. (650°C.). As transformed at this temperature level, the fine and coarse-grained

structures have hardnesses of 20 Rc and 26 Rc, respectively. The structure in either case consists of ferrite and lamellar pearlite, and the difference in hardness is due undoubtedly to the relatively smaller volume of free ferrite formed at this temperature by the coarse-grained austenite (Fig. 5).

TRANSFORMATION IN FINE-GRAINED AND COARSE-GRAINED AUSTENITE GIVEN IDENTICAL AUSTENITIZING TREATMENTS

The results of a systematic study of isothermal transformation of fine-grained and of coarse-grained austenite produced by the two austenitizing temperatures, 1550°F. (845°C.) and 2000°F. (1095°C.) have been presented. While this means of producing a difference in austenite grain size is most convenient and of greatest practical importance, there may be some doubt as to whether the large difference in the austenitizing temperature may not bring in factors other than grain size. For this reason, it is of interest to consider transformation behavior in fine-grained and coarse-grained austenite when the austenitizing treatment is the same for both.

In a single specimen it is possible to produce both fine and coarse austenite grains by selecting an austenitizing treatment that will result in a mixed grain size. For our sample of S.A.E. 4140 steel, this was accomplished by plunging each specimen into lead at 1550°F. (845°C.) and holding at this temperature for one hour; the rapid heating and the one-hour holding period combined to produce a wide range of austenite grain size in a single specimen. A photomicrograph of a specimen austenitized in this way and then partly transformed at 1200°F. (650°C.) is shown in Fig. 7. This specimen was etched to show both the austenite grain size and the amount of transformation. The large grains are essentially untransformed (martensitic), but the fine-grained areas are

about half transformed to ferrite (white) and pearlite (black).

Another method of obtaining both fine and coarse austenite grains in a single



FIG. 7.—PARTIAL TRANSFORMATION AT 1200°F. (650°C.) IN A SPECIMEN OF S.A.E. 4140 STEEL AUSTENITIZED TO PRODUCE MIXED GRAIN SIZE. $\times 150$.

Etched with grain-size reagent.

specimen is to first produce uniformly coarse grains by a high austenitizing temperature and then hot-work part of the specimen by striking it a blow with a hammer. In the hot-worked portion, the previously established coarse grains are broken up and the final condition is one of coarse austenite grains in the part of the sample that was not plastically deformed and of relatively fine grains in the deformed portion. Specimens so treated can be quenched immediately from the forging temperature into molten lead at temperatures below the A_{e1} and the subsequent transformation of the austenite can be studied in the usual way.

Both of these methods were used for studying transformation in the S.A.E. 4140 steel as it occurred at 1200°F. (650°C.) and at 700°F. (370°C.). The results were found to be indistinguishable from those

produced by different austenitizing temperatures. Thus, at 1200°F. (650°C.) transformation was found to begin and end later in the coarse-grained areas and, after transformation was complete, less free ferrite was present in the coarse-grained regions. At 700°F. (370°C.) the transformation behavior was again similar in both the fine-grained and coarse-grained areas.

On the basis of these results, it can be concluded that, in this investigation, the observed differences in the progress and result of the transformation of austenite are due to differences in austenite grain size and not to other factors associated with the austenitizing temperature.

SUMMARY

1. Increasing the austenite grain size in an S.A.E. 4140 steel from A.S.T.M. 7-8 to A.S.T.M. 2-3 greatly retards the isothermal transformation of the austenite at the higher temperature levels, about 1050°F. (565°C.) and above, where soft lamellar structures form. At lower temperature levels where the structures are acicular, grain size has no appreciable effect upon the speed of transformation of this steel.

2. The effect of grain size upon the rate of transformation to proeutectoid ferrite and lamellar products varies with the temperature level, being greatest just below the A_{e1} temperature and decreasing in intensity as the transformation temperature level approaches 900°F. (480°C.).

3. Coarse-grained austenite in S.A.E. 4140 steel tends to reject less free ferrite than fine-grained austenite at temperatures in the vicinity of 1200°F. (650°C.).

4. Microstructures resulting from transformation of coarse-grained austenite are more suitable for studying the mode of transformation and the character of the products formed than those derived from fine-grained austenite.

5. Grain size does not appreciably affect the hardness of the transformation products except at temperature levels

where there is a considerable difference in the amount of free ferrite rejected.

ACKNOWLEDGMENT

The authors are indebted to Dr. John Johnston, for advice and criticism.

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DISCUSSION

(H. J. French presiding)

H. J. ELMENDORF* AND H. A. BROWN,* Worcester, Mass.—It is interesting to observe that differences in austenite grain size do not alter the rates of austenite transformation below those temperatures at which lamellar products of austenite decomposition are formed. The authors have also shown that such changes as are found above 1050°F. are attributable only to the differences in austenite grain size.

We have investigated in a somewhat similar manner the behavior of a commercial S.A.E. 3140 steel. Our austenitizing treatments consisted of holding the specimens for 12 min. at temperatures of 1550°F., 1650°F., 1700°F. and 1800°F., and the resulting austenite grain size on the American Society for Testing Materials scale was 7-8, 6-6.5, 5-6 and 3.5-4, respectively. For the purpose of this investigation, the grain-size ratings were obtained by outlining the grain boundaries with small amounts of transformation product formed at 1050°F. Our investigation dealt only with the beginning of transformation (either to pearlite or ferrite,

* American Steel and Wire Co.

as the case may be) between 900°F. and 1100°F., inclusive. Within this range the inception of austenite transformation was found to depend wholly on the austenite grain size then

transformation rates, as well as on the types of transformation products. We have studied three widely different steels; namely, S.A.E. 4340, S.A.E. 52100, and 18-4-1 High Speed.

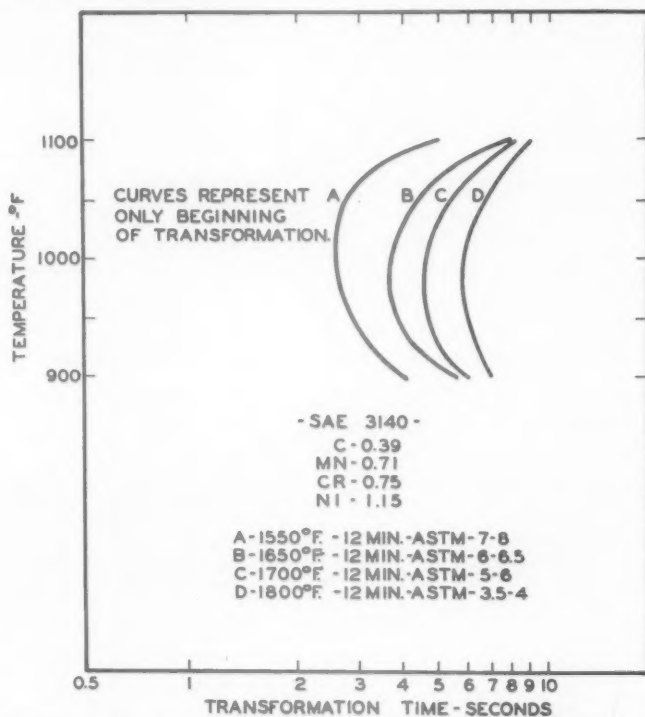


FIG. 8.—EFFECT OF AUSTENITE GRAIN SIZES ON BEGINNING OF TRANSFORMATION OF AN S.A.E. 3140 STEEL AT TEMPERATURES FROM 900°F. TO 1100°F.

existing within the untransformed austenite. Fig. 8 shows the effect of the several austenite grain sizes on the beginning of transformation of an S.A.E. 3140 steel at temperatures from 900°F. to 1100°F. We have found that the effect of austenite grain size on the start of transformation for an S.A.E. 3140 steel is noticeable at temperatures as low as 900°F. This behavior results from the general shape of the S-curve for a 3140 steel, wherein pearlite forms as low as 900°F.

P. PAYSON,* Harrison, N. J.—It is a pleasure to have another contribution from Mr. Davenport and his associates on the extremely important subject of isothermal transformation behaviors of steel. The beautiful photomicrographs of structures that are difficult to resolve are particularly gratifying.

We have been concerned for some time about the effects of austenitizing temperatures on the

The first two were austenitized at 1500°, 1800°, and 2100°F., and the latter at 1650°, 1800°, and 2350°F. We found for the S.A.E. 4340, and for the High Speed, as did the authors of the present paper for S.A.E. 4140, that increased austenitizing temperature shifted the upper portions of the transformation temperature-time curves to longer times, especially for the ends of transformation, whereas the intermediate temperature portions of the curves were almost identical for all austenitizing temperatures. On the other hand, the curves of S.A.E. 52100 were markedly affected by the austenitizing temperature, as may be seen in Fig. 9. Here, not only is the curve for the higher austenitizing temperature shifted to the right, but the shape of the curve is actually changed, the 1500°F. curve being a simple S, whereas the 1800°F. curve has a double loop.

The curve for the 2100°F. austenitizing temperature was very similar to the 1800°F. curve. Incidentally, the grain sizes were 30 per cent, 6 to 7, and 70 per cent 4 to 5, for the 1800°F.

* Eastern Research Laboratory, Crucible Steel Company of America.

GRADE SAE 52100

AUSTENITIZING TEMPERATURE --- 1500°F.
= 1800°F.

— 1800°F.

CRITICAL (A_{ci}) TEMPERATURE - 1385

PRIOR CONDITION - 1350 - 2 hr.

C

1.06

Mn

$$0.38$$

P

100

S

100

S

0.3.

Ni

1000

$$Cr$$

1.35

Mo

V

1

W

A

N

100

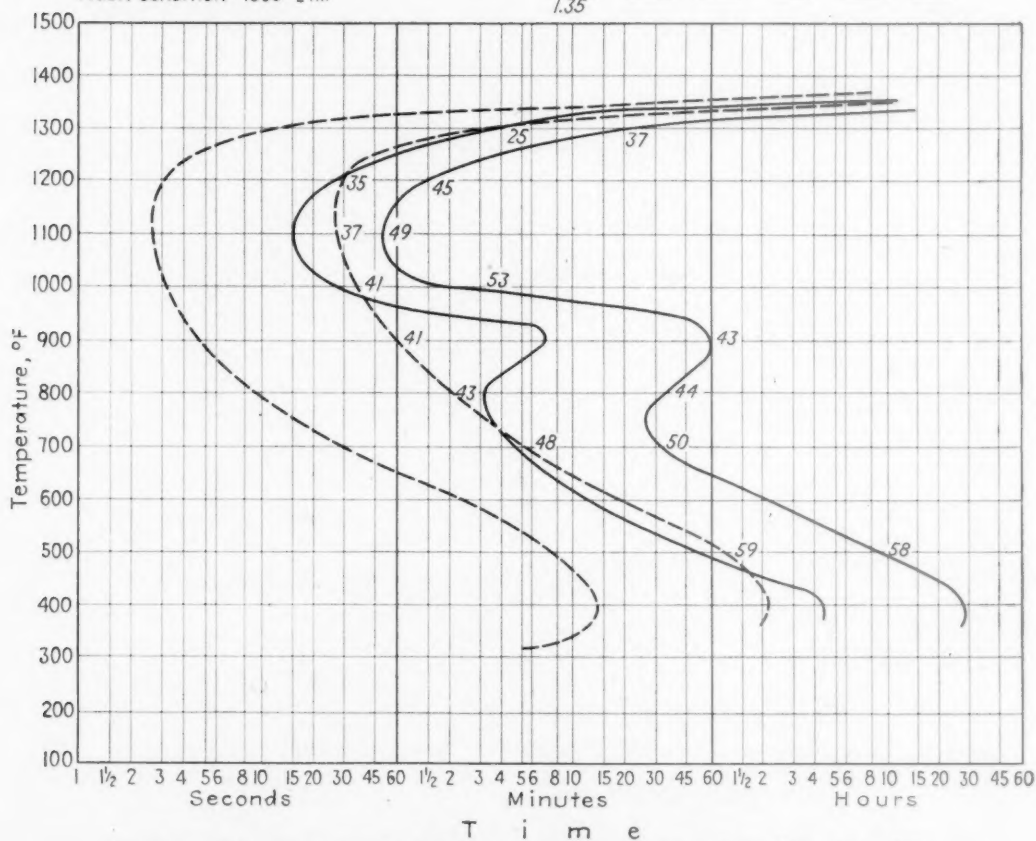


FIG. 9.—TTT CURVES OF S.A.E. 52100 AUSTENITIZED AT 1500° AND 1800°F.

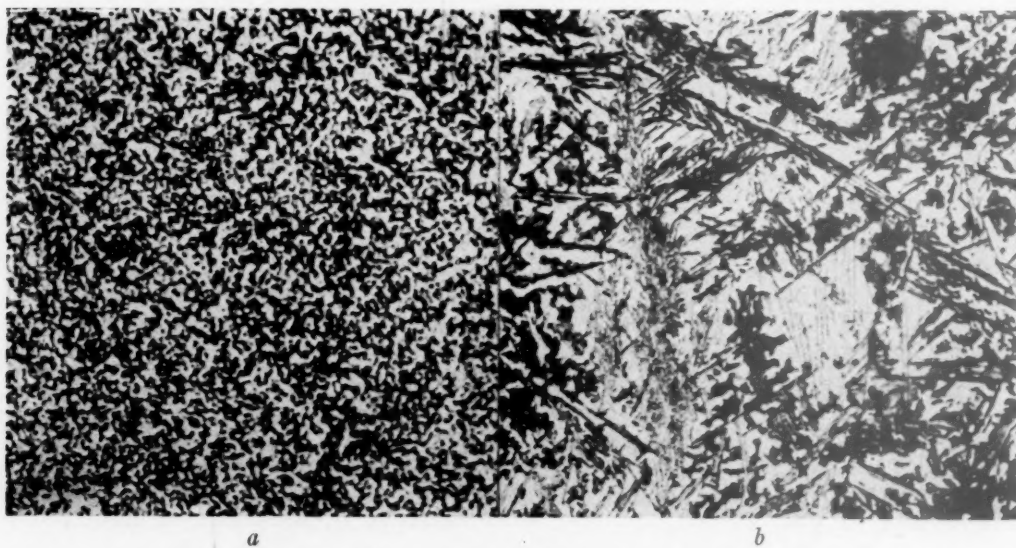


FIG. 10.—STRUCTURES OF 900°F. TRANSFORMATION PRODUCT OF S.A.E. 52100. $\times 1000$.
Left, austenitized at 1500°F.; right, austenitized at 1800°F. Nital-picral etch.

samples; and 65 per cent, 3 to 4, and 35 per cent 1 to 2 for the 2100°F. samples.

Another startling fact about the S.A.E. 52100 curves for 1800°F. and 2100°F. is that the products formed at 900°, 800°, and even 700°F. are softer than the products formed at 1100° and 1000°F., whereas the usual condition, as exemplified by the 1500°F. curve, is that the lower-temperature products are harder than the higher-temperature products.

The structures obtained at intermediate temperatures also are quite different, depending on the austenitizing temperature, as may be seen in Fig. 10. The product formed at 900°F. is granular for the sample austenitized at 1500°F., and—for want of a better name—nondescript for the sample austenitized at 1800°F. A structure very similar to the latter was obtained in the 2100°F. sample.

We may conclude from these observations that as long as the composition of the austenite is not much affected by the austenitizing temperature, the transformation rates and products are not much altered. In the S.A.E. 4140 discussed by the authors, and the S.A.E. 4340 studied by us, the austenite, for all conditions studied, was a solid solution with no excess constituent. In the High Speed, the austenite undoubtedly had more carbide in solution at 2350°F. than it had at 1650°F., but excess carbides existed at all temperatures. The austenite of the S.A.E. 52100, on the other hand, had all carbides in solution at 1800° and 2100°F., but was of much lower carbon content at 1500°F., since there were many excess carbides at this temperature, and therefore it is not altogether surprising that the higher-temperature austenites of this steel behaved differently from the lower-temperature austenite.

There is one field of transformation which the authors apparently have not surveyed, and that is the region close to room temperature. When a piece of steel is quenched so as to avoid transformations in the upper and intermediate regions, it will transform at temperatures from about 300°F. down to room temperature. It would, of course, be interesting to know how austenitizing temperature affects the transformations in this very important region, and it is hoped that the authors will soon have some data to present on this subject.

G. SACHS,* Cleveland, Ohio.—Is there an explanation for the knee in the S-curves at

approximately 1000°F.? This knee seems dependent upon the presence of carbide-forming elements, which, if so, indicates a relation between the presence of such a knee and the precipitation of special carbides from martensite on tempering a quenched steel.

I wonder, therefore, whether the decomposition of the austenite at these temperatures might not be a complicated process in which ferrite is first formed followed by the transforming of the eutectoid austenite into some type of alpha solid solution from which the carbides eventually precipitate. Is it possible to determine experimentally whether such a multistage reaction exists?

E. S. DAVENPORT, R. A. GRANGE AND R. J. HAFSTEN (authors' reply).—Messrs. Elmendorf and Brown have submitted an interesting example of the influence of austenite grain size upon transformation in a medium-carbon, nickel-chromium steel of the S.A.E. 3140 type. We also studied isothermal transformation in an S.A.E. 3140 steel having a chromium content of about 0.5 per cent, which is somewhat lower than in the material studied by Elmendorf and Brown. In our work on 3140 a retardation was observed in the transformation at the 900°F. and the 1000°F. temperature levels, as well as at higher temperatures, and this retardation increased as the austenite grain size increased from 7-8 to 2; however, the displacement of the curve representing the visible beginning of transformation in the 900° to 1000°F. temperature range was considerably less than that reported by Elmendorf and Brown. For our difference of 5 to 6 A.S.T.M. numbers we found no more displacement in the beginning line than they observed for a difference of only two grain-size numbers. It should be mentioned that the line for beginning of transformation, when it lies to the left of 5 sec., is usually the least precise portion of the diagram and rather large discrepancies may be expected in the results obtained by different observers, even when working with the same steel.

The fact that transformation at 900°F. was retarded by coarsening the austenite grains in our S.A.E. 3140 steel, even though we found the structure to be what we prefer to call high-temperature bainite rather than pearlite, as

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reported by Elmendorf and Brown, is not surprising, since we observed, in this steel, a tendency toward preferential transformation at the austenite grain boundaries; that is, after partial transformation had occurred at 900°F., the austenite grains were outlined by a network of transformation product. It is our experience that grain size affects the rate of isothermal transformation at all temperature levels except those at which a random distribution of distinct bainite needles, entailing no preference for transformation at the austenite grain boundaries, is produced; this is consistent with the observation that, in general, the higher the transformation temperature the greater the influence of grain size.

Mr. Payson's comprehensive discussion indicates that he has been actively engaged in the study of isothermal transformation. The conclusions he reaches concerning the influence of austenite grain size upon transformation behavior seem to confirm our own, even though he studied quite different types of steel.

His data for the S.A.E. 52100 steel are especially interesting since they are different, in some respects, from any that have thus far been published. As Mr. Payson points out, increasing the austenitizing temperature may affect transformation in two major ways: (1) by coarsening the austenite grains, and (2) by dissolving more of the carbides, thus increasing the amount of alloying elements dissolved in the austenite. For the higher-carbon grades of steel, this latter effect is of the utmost significance at the relatively low austenitizing temperatures used in practice. For example, a steel like S.A.E. 52100 requires high temperatures to dissolve all the carbides and, until they are dissolved, the effective chemical composition of the austenite changes with each different austenitizing treatment; furthermore, until the carbides are substantially all in solution, no appreciable coarsening of the austenite grains is likely to occur. The question of homogeneity or uniform distribution of carbon and alloying elements in the austenite is perhaps of less importance, but should not be entirely overlooked.

The reversal in the trend of increasing hardness with decreasing transformation temperature which Mr. Payson observed in the S.A.E. 52100 steel, austenitized at either 1800°F. or 2100°F., is surprising, not because of the fact that there was a reversal but because it was of

such a high order of magnitude. We have observed similar reversals of hardness in other alloy steels, but rarely have they been as marked as that reported by Mr. Payson. Another interesting point is the relatively high order of hardness reported for the products of transformation at temperatures of 1000°F. and above in this 52100 steel as austenitized at 1800°F.; for this particular steel, hardness of the isothermal transformation products in this temperature range appears to increase with the amount of carbon in solution at the austenitizing temperature. Judging from the character of the microstructure at 900°F., the relatively low hardness of structures formed in the vicinity of this temperature level, as austenitized at 1800°F., is understandable. This structure differs markedly from the 900°F. product in the same steel austenitized at 1500°F. where all the carbides were not in solution; this is probably due almost entirely, as Mr. Payson implies in his discussion, to the difference in chemical composition of the austenite in the two cases rather than to the influence of austenite grain size.

We agree with Mr. Payson that it would be very interesting to know how austenitizing temperature effects transformation at relatively low temperatures where martensitic products form. We have made some attempts to determine the influence of grain size upon transformation to martensite, but do not feel warranted in drawing any conclusions at this time. Certainly this phase of the problem provides an excellent field for further research.

With respect to the very pertinent questions posed by Dr. Sachs, we believe the simplest explanation for the so-called "knee" in the S-curves in the vicinity of 1000°F. is that the carbide-forming elements produce this "knee" by retarding transformation to a vastly greater extent above about 1000°F. than below. The exact mechanism of the transformation reaction at about 1000°F. is still, so far as we are concerned, an inadequately explored process; however, there is evidence both from microscopic and dilatometric observations that the reaction does take place in a series of stages in this temperature range, involving some such process as that suggested by Dr. Sachs; this subject is discussed in some detail in the 1939 Campbell Lecture.*

* *Trans. Amer. Soc. Metals* (1939) 27, 837-886.

Rate of Diffusion of Manganese in Gamma Iron in Low-carbon and High-carbon Manganese Steels

BY CYRIL WELLS* AND ROBERT F. MEHL,† MEMBERS A.I.M.E.

(New York Meeting, February 1941)

THE practical importance of a knowledge of the rates of diffusion of carbon and of alloying elements in steel has often been pointed out.^{1,13} This importance lies chiefly, though by no means only, in the study of carburizing and in the study of reactions involved in the eutectoid inversion in steel. The present paper is one of a series in which the rates of diffusion of carbon and of alloying elements in γ -Fe and their mutual effects are measured with precision. The present paper reports the results of measurements of diffusion coefficients D of manganese in γ -Fe over wide ranges of temperature, and concentration, and of the effect of carbon and impurities and of grain size upon these diffusion coefficients.†

Data on the rate of diffusion of manganese in γ -Fe have been reported by Fry² and by Paschke and Hauttmann.³ Claussen⁴ calculated the diffusion coefficient D from Fry's data as 3×10^{-10} sq. cm. per sec. at 960° , which will be shown to be incorrect by many orders of magnitude. Paschke and Hauttmann gave a rough value of 9.6×10^{-8} sq. cm. per sec. at 1400° . Neither of these workers considered the variation of D with concentration and with temperature, and neither studied the effect of carbon.

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¹ References are at the end of the paper.

‡ The effect of manganese (and nickel) on the rate of diffusion of carbon in austenite was reported in an earlier paper.⁵

METHOD AND MATERIALS

Method.—The method employed is identical with that used earlier.⁵ Owing to the volatility of manganese and the consequent loss of manganese from the outer surfaces of the welded diffusion bars, these surfaces were discarded. The diffusion anneals were performed in argon, except one (test 18) in which hydrogen was employed for purposes noted below. The temperatures reported are accurate to about 3° and constant within 1°C. ; the diffusion times are reported to the nearest half hour. The specimens were furnace-cooled after the diffusion anneal at about 2° per min. Layers, usually 0.004 in. thick, parallel to the welded interface, were machined from the specimens after the diffusion anneal and analyzed for manganese to 0.1 per cent Mn; the distances of these layers from the interface was measured to ± 0.0002 in. The concentration-penetration curves obtained were analyzed by both the Grube and the Matano solutions.⁸ The D values calculated by these two methods do not differ appreciably.⁵ The Grube solution was used except in tests in which the effect of concentration upon D was greater than 50 per cent; in such cases the Matano method, which explicitly provides for the variation of D with concentration,¹ is the more reliable. In general, the number of layers machined from the zones of variable composition were large enough to permit the use of the average layer composition as that of the center of the layer. In 3 of the 30 tests, however, this is not justified, and the D values

in these tests were determined by a trial and error method, consisting of plotting concentration-penetration curves and assuming D values; these D values were taken to be correct within experimental error when the calculated average manganese compositions of consecutive layers in a specimen having the assumed D values were the same as those obtained by analysis.

does not give accurate results for steels containing high manganese, but it is believed that the figures given in the table are correct within about an order of magnitude.

MICROSTRUCTURES

The position of the weld zones could ordinarily be seen only after etching. The photomicrographs of Fig. 1 give evidence

TABLE I.—Composition of Alloys

Alloy No.	Composition, Weight Per Cent									
	Mn	C	Si	P	S	Cu	Ni	O ₂	N ₂	H ₂
1B	16.0	0.02	0.005	<0.005	0.005	0.012	0.003	0.003 0.010	<0.001 0.018	0.0004 <0.0001
2A	1.0	0.02								
3B	16.3	1.35				0.032	0.009			
4A	2.5	1.2				0.012	0.002			
5A ^a	0.0	0.01				0.006	0.040			
6A	2.2	0.01								
7B	16.1	0.31								
8A	2.0	0.35								
9B	20.2	0.02						0.016 ^b	0.053	<0.0001
10A	10.1	0.04				0.01	<0.005	0.003	0.037	<0.0001
10B	10.1	0.04	0.68 1.39	0.071 0.015	0.017 0.012	0.01	<0.005	0.003	0.037	<0.0001
11B	35.7	0.01								
12A	30.1	0.01								
13B	47.7	0.02								
14A	0.0	0.02				0.036	0.010	0.003	0.001	<0.0001
15B	59.9	0.03								
16B	53.5	0.003								
17B	12.6	1.20								
18A	0.5	1.02								
19A	4.4	0.02	0.005	<0.005	0.005	0.008	<0.005	<0.005		
20B	13.2	0.24				0.009	<0.005			
21A	1.9	0.32								
22B	13.1	0.29								
23A	3.9	0.25								

^a Chromium, tin and molybdenum were present as spectroscopic traces. In similar iron these elements taken together gave a total of less than 0.005 per cent.

^b Oxygen analyses for the high-manganese alloys are of doubtful accuracy.

Materials.—The composition of the materials used in the present investigation are given in Table I. Alloys 1B to 16B inclusive and 19A to 21A are high-purity alloys made by melting distilled manganese with vacuum-melted electrolytic iron. Some of these are unusually high in nitrogen. Iron 5A is a carbonyl iron hydrogen-treated for 750 hr. at 1200°C. Of the remaining alloys 17B is a Hadfield steel of commercial grade, 18A is a steel used in the manufacture of malleable iron, while 22B and 23A are of commercial purity and made in a small 250-lb. arc furnace. Oxygen analyses were made by the vacuum-fusion method, which

of good welds in a specimen (Fig. 1a) containing 10 per cent Mn, 0.04 per cent C at one end (upper) and 0 per cent Mn, 0.01 per cent C at the other end (lower); and in a specimen (Fig. 1b) containing 16 per cent Mn, 1.35 per cent C at one end (upper) and 2.5 per cent Mn, 1.2 per cent C at the other end (lower). These photomicrographs also show that the interface is sharp and that the extent of penetration of manganese into the iron during welding is therefore inappreciable. Typical microstructures across diffusion zones before and after the diffusion anneal are shown in Figs. 1c and 1d and Figs. 2a and 2b.

RESULTS

Diffusivity coefficients at various concentrations are listed in Table 4. The original experimental data used in the determination of concentration-penetration curves and from which D values have been calculated are given in Table 3.*

mination of diffusivity coefficients and of the precautions taken to guarantee maximum accuracy have been given in an earlier publication;⁵ it will be noted that good reproducibility is obtained in check tests (tests 11 and 13, Table 4, 4 and 6, Table 5) and that the experimental points of Fig. 4

TABLE 2.—Heat-treatment and Grain Size

Test No.	Alloys Welded	Temperature of Diffusion, Deg. C.	Time of Diffusion, Hr.	Range of Carbon Content, Wt. Per Cent			Average Number of Austenite Grains per Sq. Mm.	
				Before Test	After Test	Assumed Average	Alloy A	Alloy B
1	4A-3B	1000	240	1.2-1.35	1.20	1.24	8	<1
2	6A-1B	1050	1344	0.01-0.02	0.51	0.26	16 ^c	2
3	4A-3B	1050	1344	1.2-1.35	1.0	1.14	2	2
4	2A-1B	1100	333	0.02-0.02	0.21	0.12	<1	2
5	6A-9B	1100	1000	0.01-0.02	0.01	0.01	16 ^c	32
6 ^b	8A-7B	1100	1000	0.35-0.31	0.13	0.23	2	4
7	4A-3B	1100	333	1.2-1.35	1.08	1.18	2	2
8	6A-10B	1155	503	0.02-0.04	0.55	0.29	<1	64
9	2A-1B	1200	197.25	0.02-0.02	0.20	0.11	<1	<1
10	6A-9B	1200	250	0.01-0.02	0.01	0.01	<1	8
11	10A-11B	1200	480	0.04-0.01	0.02	0.02	<1	<1
12	12A-13B	1200	480	0.01-0.02	0.01	0.01	4	<1
13	14A-15B	1200	480	0.02-0.03	0.02	0.02	<1	20
14	4A-3B	1200	106	1.2-1.35	1.53	1.4	<1	<1
15	4A-3B	1200	197.25	1.2-1.35	1.22	1.25	<1	<1
16	4A-3B	1200	250	1.2-1.35	1.51	1.4	1	2
17	14A-10B	1250	230	0.02-0.04	0.02	0.02	<1	16
18	6A-10B	1250	246	0.02-0.04	0.01	0.01	<1	32
19	5A-1B	1250	329	0.01-0.02	0.01	0.01	<1	<1
20	2A-1B	1250	1174	0.02-0.02	0.02	0.02	<1	<1
21	21A-20B	1250	240	0.32-0.24	0.30	0.29	4	4
22	23A-22B	1250	240	0.25-0.29	0.29	0.28	1	4
23	18A-17B	1250	221	1.02-1.20	0.53	0.82	8	<1
24	4A-3B	1250	240	1.2-1.35	0.70	0.97	16	16
25	6A-9B	1300	96	0.01-0.02	0.21	0.11	<1	8
26	14A-10B	1350	105	0.04-0.02	0.02	0.02	<1	8
27	6A-9B	1350	72	0.01-0.02	0.26	0.15	<1	2
28	8A-7B	1350	72	0.35-0.31	0.26	0.29	<1	1
29	6A-9B	1400	51	0.01-0.02	0.04	0.02	<1	<1
30	19A-10B	1450	50	0.02-0.04	0.03	0.03	2	2

* Analysis of alloys given in Table 1.

^b Furnace tube cracked; considerable carbon was lost from specimen during test.

^c These are ferrite grain sizes.

TABLE 3. See footnote below.

Accuracy.—The D values recorded in Table 4 are believed to be correct to within ± 15 per cent. A detailed discussion of the factors that affect the accuracy of the deter-

are all close to straight lines. D values were determined in test 17 to compare with the values obtained in tests 19 and 20 in order to show whether or not it is necessary to homogenize the iron-manganese alloys prior to the diffusion anneal. Apparently the preliminary high-temperature treatment of 65 hr. at 1425°C. in test 17 had no effect on the D value obtained. Since the heterogeneity in an alloy with much higher manganese was largely removed (Figs. 2c and 2d) by a less severe treatment than that

* Table 3 has been issued through auxiliary publication and may be obtained from the American Documentation Institute, care Science Service, 2101 Constitution Avenue, Washington, D. C., by ordering. Document No. 1485, remitting 26¢ for copy in microfilm (images 1 in. high on standard 35-mm. motion picture film) or 80¢ for copy in paper photo-prints legible without mechanical aid.

given the high-manganese specimen 17, it is assumed that the latter was effectively homogenized.

Effect of Concentration of Manganese and Carbon on D .—The effect of manganese

content increases about 125 per cent as the manganese content is raised from close to 0 to 60 per cent, and this increase is almost linear with concentration. This increase in the percentage of D is approximately

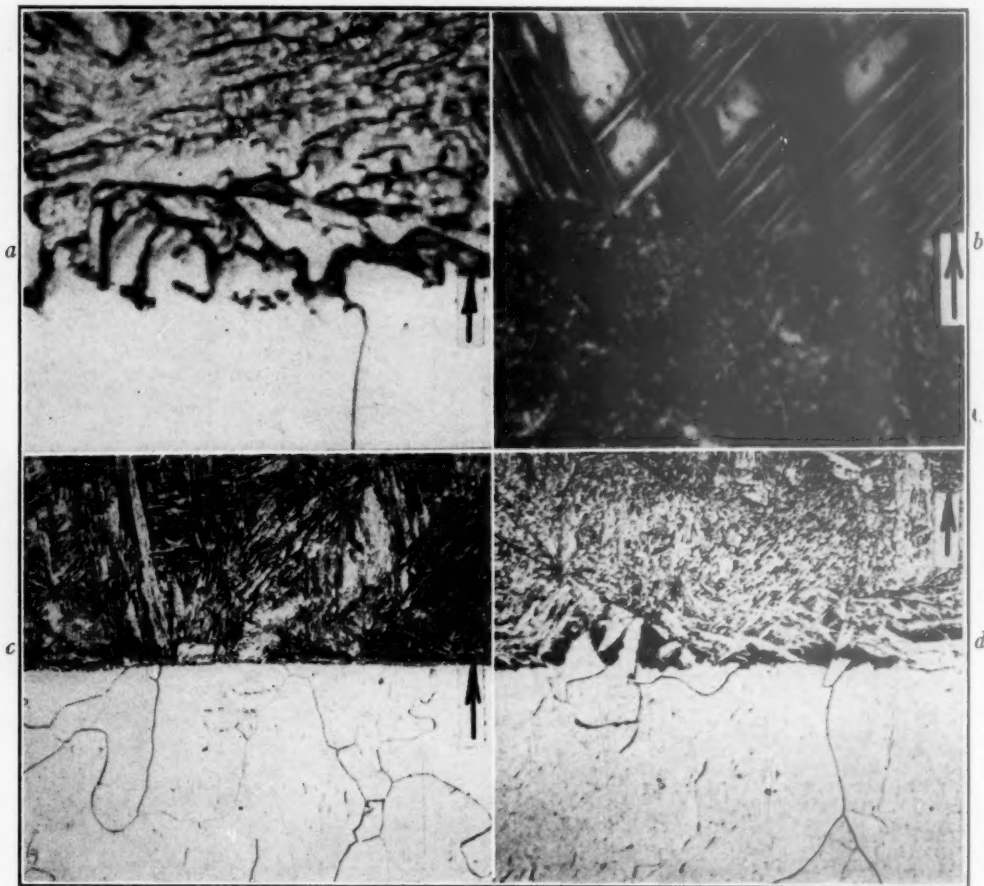


FIG. 1.—EVIDENCE OF GOOD WELDS (*a* AND *b*) AND MICROSTRUCTURES OF DIFFUSION ZONES BEFORE (*c*) AND AFTER DIFFUSION ANNEALING (*d*). POSITIONS OF ORIGINAL WELDS ARE INDICATED BY ARROWS.

a, alloy with 10 per cent Mn, 0.04 per cent C (upper) welded to high-purity iron (lower). $\times 2000$.

b, alloy with 16 per cent Mn, 1.35 per cent C (upper) welded to one with 2.5 per cent Mn, 1.2 per cent C. Tempered after welding. $\times 2000$.

c, same as *a*, but $\times 100$.

d, same as *c* except that specimen was heated at 1250°C . for 230 hr. $\times 100$.

All specimens were etched with 4 per cent Nital.

concentration on the rate of diffusion of manganese is shown in Fig. 5 and the effect of carbon on the rate of diffusion of manganese in Figs. 5 and 6. These results show that D increases with increasing manganese and that carbon increases the rate of diffusion of manganese. The diffusivity coefficient

increases about 125 per cent as the manganese content is raised from close to 0 to 60 per cent, and this increase is almost linear with concentration. This increase in the percentage of D is approximately

independent of carbon up to 1.25 per cent, though the rate of diffusion at a given manganese content is markedly affected by carbon content.

Increasing the carbon content from below 0.02 to 1.25 per cent raises the D value at 1200°C . from about 10 to 40×10^{-11} sq.

cm. per sec., i.e., by about 300 per cent (Fig. 6). The dashed curve, which shows the relationship between carbon content and the percentage increase of D at temperatures between 1050° and 1250°C., indicates

carbon concentrations. These data are listed in Table 5; those used in the plot of $\log D$ versus $\frac{1}{T}$ (Fig. 4) are referred to in note c of the same table.

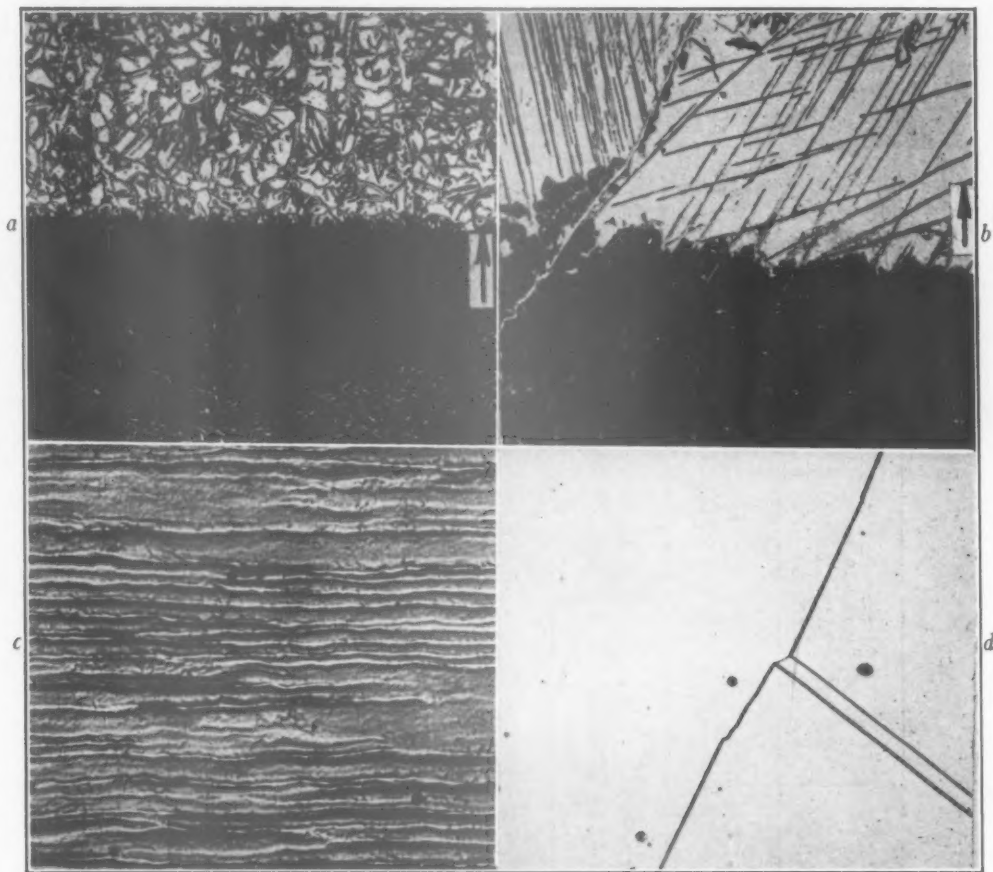


FIG. 2.—MICROSTRUCTURES BEFORE (a) AND AFTER DIFFUSION ANNEALING (b), AND STRUCTURES IN A FORGED ALLOY BEFORE (c) AND AFTER HOMOGENIZING (d). POSITION OF WELD IN a AND b SHOWN BY ARROWS.

a, alloy with 16 per cent Mn, 1.35 per cent C (upper), welded to one with 2.5 per cent Mn, 1.2 per cent C (lower).

b, same as a except that specimen was heated 96 hr. at 1250°C. and furnace-cooled.

c, alloy with 54 per cent Mn, 0.02 per cent C, as forged.

d, same as c but homogenized. Heated at 1260°C. for 240 hr.

Etchant was 4 per cent Nital, and magnification $\times 100$.

that the percentage increase of D is approximately independent of temperature.

Effect of Temperature on D .—From the known relationship between the percentage increase of D and carbon content (Fig. 6) calculations were made to determine D values at 0.02 and 1.25 per cent C, respectively, from known D values at other

The relationship between temperature and the rate of diffusion of manganese at manganese concentrations of 4 and 14 per cent and at carbon concentrations of 0.02 and 1.25 per cent, respectively, is given in Fig. 4. At low carbon concentrations (below 0.02 per cent) the range covered in tests is about 400°C. (1050° to 1450°C.) and at high

carbon concentrations it is 250°C. (1000° to 1250°C.). The dashed line was determined from a known rate of diffusion at 60 per cent Mn in a high-manganese low-carbon alloy at 1200°C. and the Dushman-Langmuir equation. The log D versus $\frac{1}{T}$ point was plotted and the slope of the line

Effect of Impurities.—Occasionally evidence of slight oxidation was found in low-carbon specimens heated in argon. In order to determine whether or not such small amounts of oxygen affected the measured rate of diffusion of manganese, specimen 18, test 18, was given the diffusion anneal in hydrogen instead of in argon; the D value

TABLE 4.—Diffusion Data, Manganese in Gamma Iron

Test No.	Manganese Range in Specimen, Wt. Per Cent	Temperature of Diffusion, Deg. C.	Carbon ^a Content, Per Cent	$D \times 10^{11}$ Sq. Cm. per Sec. at Various Mn Concentrations, Atomic Per Cent ^{b,f}				
				4 %	14 %	34 %	44 %	58 %
1	2.5-16.3	1000	1.24	1.6	1.8			
2	2.2-16.0	1050	0.26	0.1	1.6			
3	2.5-16.3	1050	1.14	3.2	3.2			
4	1.0-16.0	1100	0.12	2.05	2.6			
5	2.2-20.2	1100	0.01	1.7	2.0			
6	2.0-16.1	1100	0.23	(2.3) ^c	(2.3)			
				2.2	2.7			
7	2.5-16.3	1100	1.18	6.9	7.9			
8	2.2-10.1	1155	0.29	6.3				
9	1.0-16.0	1200	0.11	(13)	(15)			
				12	14			
10	2.2-20.2	1200	0.01	9.8	10.2			
11	10.1-35.7	1200	0.02		10.0			
12	30.1-47.7	1200	0.01			13		
13	0.0-59.9	1200	0.02	8.0	10.1	18	20	
				(9.8)	(11.0)	13.0	14.3	19.6
						(12.7)	(17.1)	(21.6)
14	2.5-16.3	1200	1.4	43	62			
15	2.5-16.3	1200	1.25	41	46			
16	2.5-16.3	1200	1.4	43	54			
17	0.0-10.1	1250	0.02	19				
18 ^d	2.2-10.1	1250	0.01	24				
19	0.0-16.0	1250	0.01	17	20			
20	1.0-16.0	1250	0.02	21	23			
21	1.9-13.2	1250	0.29	32				
22	3.9-13.1	1250	0.28	31 ^e				
23	0.5-12.6	1250	0.82	66				
24	2.5-16.3	1250	0.97	(56)	(65)			
				59	67			
25	2.2-20.2	1300	0.11	39	53			
26	0.0-10.1	1350	0.02	73				
27	2.2-20.2	1350	0.15	83	99			
28	2.0-16.1	1350	0.29	92	113			
29	2.2-20.2	1400	0.02	121				
30	4.4-10.1	1450	0.03	263 ^g				

^a These data are taken from Table 2, column 7.

^b Equivalent weight per cent values are slightly lower, but the difference is insignificant.

^c The Matano method was used to calculate all D values in parentheses and the Grube method to calculate all other values.

^d Specimen 18, test 18, was heated in hydrogen. All other specimens were heated in argon.

^e These figures are the values at 6 atomic per cent Mn, but they would be the same at 4 per cent within experimental error.

^f In the calculation of D values, account was taken of the fact that the concentration gradients across the diffusion zones at diffusion temperatures and room temperatures, respectively, are different.

through the point was determined from the Q value calculated from the Dushman-Langmuir equation. Because of doubts relating to the validity of this equation, the slope may be questioned, but in view of the slopes of the full lines above and below, the slope of the dashed line looks quite reasonable.

was found to be 24×10^{-11} sq. cm. per sec. at 4 per cent Mn as against 19×10^{-11} sq. cm. per sec. for the specimens heated in argon (the average value of tests 17, 19, and 20). Oxygen (or hydrogen) in amounts present in specimens used in this investigation has apparently little effect on D . Most of the difference observed may be due to

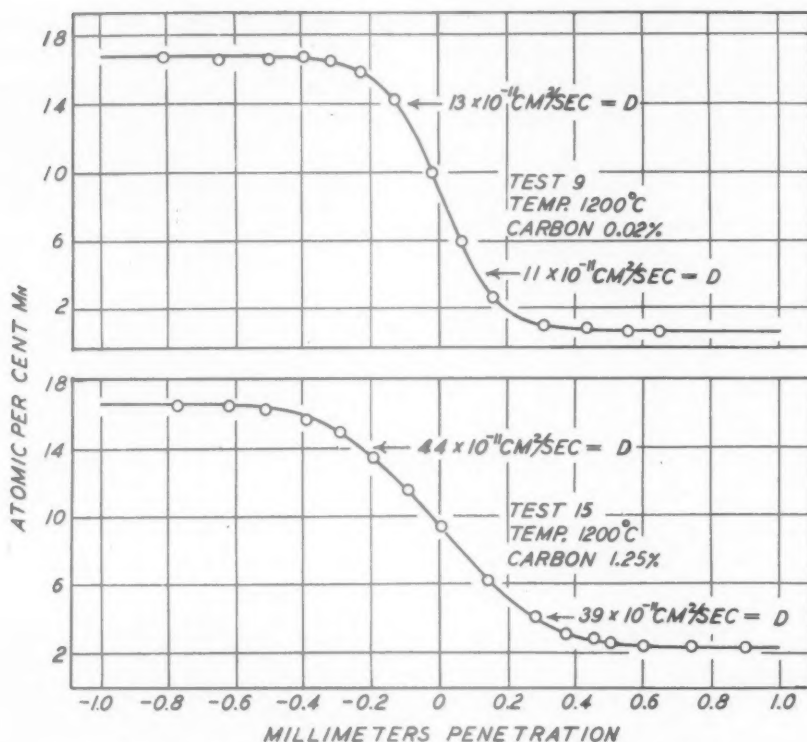
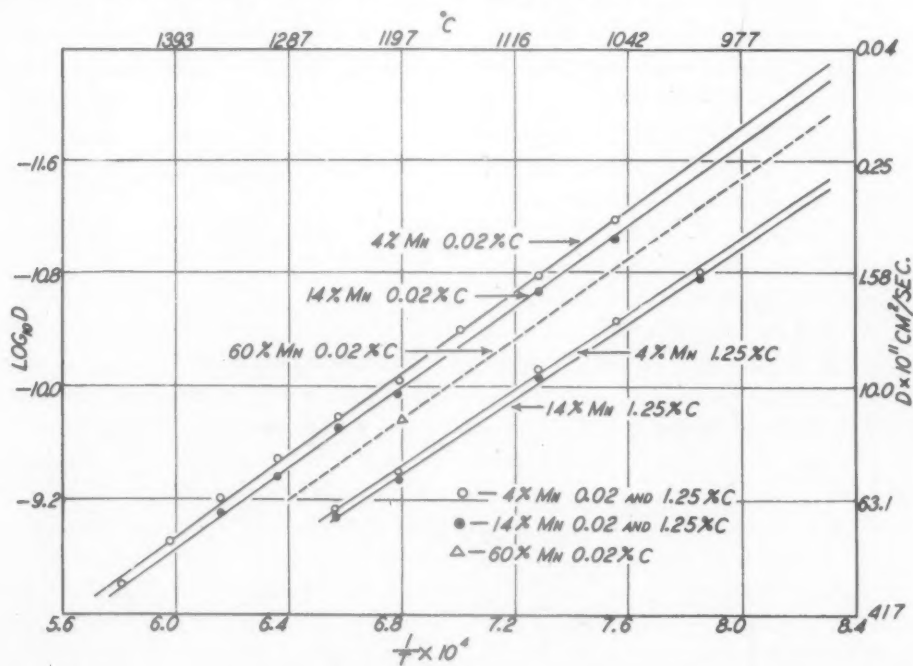


FIG. 3.—TYPICAL CONCENTRATION-PENETRATION CURVES.

Showing (a) all data points to fall on or close to the curves and (b) carbon to increase the rate of diffusion of manganese in austenite. Time of heating 197.25 hours.

FIG. 4.—PLOT OF $\log_{10} D$ VERSUS $1/T$ (T IN ABSOLUTE DEGREES), AT VARIOUS CONCENTRATIONS.

Scales of D in square centimeters per second and of temperature in degrees centigrade also included.

experimental error, which may amount to ± 15 per cent, and in extreme cases account for a difference of 30 per cent in the value of D determined in comparable tests.

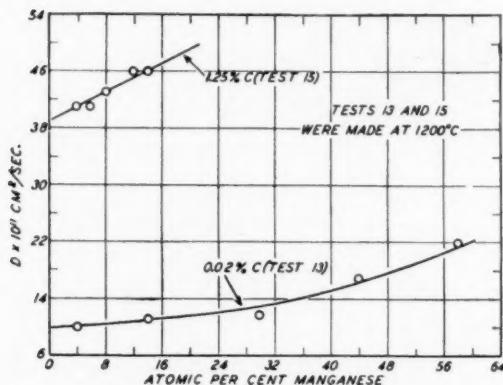


FIG. 5.—DIFFUSION COEFFICIENT PLOTTED AS FUNCTION OF MANGANESE CONCENTRATION.

The silicon content of commercial Hadfield steel lies between 0.3 and 1 per cent. It is desirable, therefore, to appraise the effect of silicon upon the rate of diffusion of manganese. In test 23 the specimen consisted of Hadfield steel containing 12.6 per cent Mn, 1.2 per cent C and 0.68 per cent Si, welded to a steel with 0.5 per cent Mn, 1.02 per cent C and 1.39 per cent Si. The D value at 4 per cent Mn is 66×10^{-11} sq. cm. per sec.; corrected from the data on the variation of D with the percentage of carbon, this gives 87×10^{-11} sq. cm. per sec. at 1.25 per cent C. The value of D found for similar compositions in high-purity iron-manganese-carbon alloys is 74×10^{-11} sq. cm. per sec. (test 24, Table 5). Apparently 1 per cent Si has little or no effect on the rate of diffusion of manganese in γ -Fe. A similar conclusion may be drawn from the results of tests 21 and 22; specimen 21 consisted of high-purity alloys having less than 0.005 per cent Si, one alloy having 0.24 per cent C and 13.2 per cent Mn and the other 0.32 per cent C and 1.9 per cent Mn; specimen 22 consisted of two alloys, each containing 0.27 per cent Si, one alloy having 0.29 per cent C and 13.1 per cent Mn, and the other 0.25 per cent C and

3.9 per cent Mn. The D values determined in these tests were 32×10^{-11} and 31×10^{-11} sq. cm. per sec., respectively.

TABLE 5.—Diffusion Data, Manganese in Gamma Iron
At 4 and 14 Atomic Per Cent Manganese,^a
and at 0.02 and 1.25 Weight Per Cent Carbon

Test No.	Temperature, Deg. C.	$D \times 10^{11}$ Sq. Cm. per Sec. ^b at 4 At. Per Cent Mn and		$D \times 10^{11}$ Sq. Cm. per Sec. at 14 At. Per Cent Mn and	
		0.02 Per Cent C	1.25 Per Cent C	0.02 Per Cent C	1.25 Per Cent C
1 ^c	1000		1.6		1.8
2	1050	0.68		0.92	
3	1050		3.4		3.4
4	1100	1.7		2.2	
5	1100	1.7		2.0	
6	1100	1.6		2.1	
7	1100		7.6		8.6
8	1155	4.0			
9	1200	9.5		11.6	
10	1200	9.8		10.2	
13	1200	(9.8)		(11.0)	
14	1200		41		58
15	1200		41		46
16	1200		41		50
17	1250	19			
18	1250	24			
19	1250	17		20	
20	1250	21		23	
23	1250		87		
24	1250		74		84
25	1300	33		43	
26	1350	73		80	
27	1350	63			
29	1400	121			
30	1450	263			

^a Equivalent weight per cent values are slightly lower, but the difference is insignificant.

^b The D values are obtained by taking data from Table 4 and by use of Fig. 6.

^c Data from tests 1 to 4, 7 to 9, 15, 19, 24, 25, 27, 29, and 30 were used in the determination of the log D versus $1/T$ curves of Fig. 4.

In tests 21, 22, 23 and 24, it may be noted that specimens 22 and 23 (commercial alloys) contained up to 0.071 per cent P and 0.017 per cent S, and that the specimens 21 and 24 (high-purity alloys) contained less than 0.005 per cent each of these two elements; since the D values are substantially the same in all the tests irrespective of impurities, it is unlikely that P and S in the amounts given have much effect.

The effect of 0.0004 per cent H on D is assumed to be negligible for it is difficult to

believe that it could be otherwise; on the other hand 0.05 per cent N, an amount present in alloy 9B (Table 1), may be expected to have a slight effect about equal

austenite grain boundaries in the diffusion zone. The minute irregularities in the regions of marked change of structure are believed to result primarily from grain

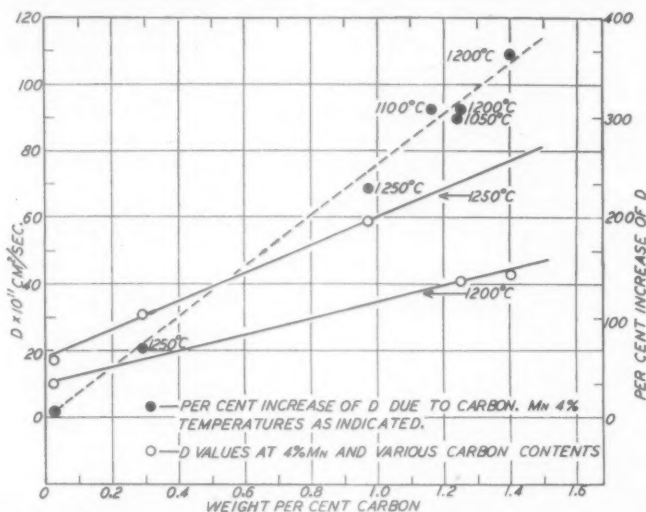


FIG. 6.—RATE OF INCREASE OF D WITH CARBON CONTENT SHOWN TO BE ROUGHLY LINEAR AND PERCENTAGE RATE OF INCREASE OF D TO BE APPROXIMATELY INDEPENDENT OF TEMPERATURE (DASHED CURVE).

to that of a similar amount of carbon since the D values of carbon and nitrogen in γ -Fe are similar.

Effect of Grain Size.—It was hoped that manganese could be diffused in specimens with large and small grains, respectively, and the influence of grain size on the rate of diffusion of manganese determined directly.⁵ Unfortunately, however, at temperatures at which sufficient diffusion occurs to give reliable results, the grains are always large, and it is doubtful whether an appreciable amount of manganese traversed more than two or three grains in any of the tests. For this reason any information regarding the influence of grain size on D must be inferred from results of the microscopic studies.

Typical microstructures across diffusion zones are shown in Fig. 1d and Fig. 2b. These structures give the general impression that the "diffusion front" of a given manganese concentration in the diffusion zone cuts the plane of polish to give straight traces, irrespective of the presence of

change during transformation on cooling; the fine pearlite nodules in close proximity to the former austenite grain boundary (Fig. 3b) on similar reasoning do not indicate a grain-size effect. It appears, therefore, that grain size has little or no effect on the rate of diffusion of manganese.

Q and A Values.—The diffusion equation is generally written:

$$D = A \times e^{-\frac{Q}{RT}}$$

where A and Q are constants at a given concentration and D is a constant at a given temperature and concentration. Q is the activation heat of diffusion, T the absolute temperature and R the gas constant. In the data given herewith, D and A are expressed in square centimeters per second, Q in gram calories per gram atom, T in absolute degrees and R in gram calories per degree centigrade per gram atom.

Q has been calculated at 4 and 14 per cent Mn in alloys containing 0.02 and 1.25

per cent C, respectively, from the slopes of the full straight lines in Fig. 4.

In low-carbon high-manganese alloys containing less than 0.02 per cent C, the Q

with those calculated from the $\log_{10} D$ vs. $1/T$ curve; in view of this it may be permissible to apply it to a manganese concentration above 20 per cent at which too

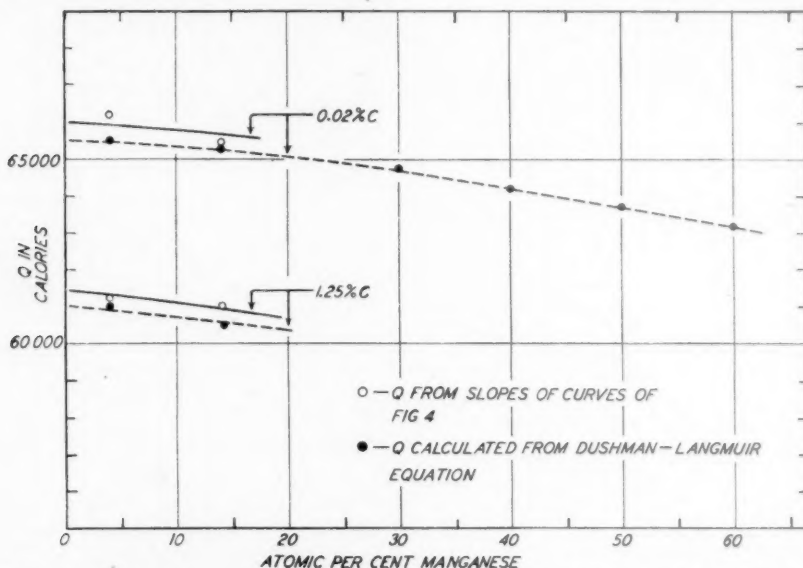


FIG. 7.—RELATIONSHIP BETWEEN Q AND MANGANESE CONCENTRATION IN LOW-CARBON AND HIGH-CARBON IRON-MANGANESE-CARBON ALLOYS, RESPECTIVELY.
 Q (activation heat of diffusion) given in gram calories per gram atom.

values are 66,200 and $65,400 \pm 500$ cal. at manganese concentrations of 4 and 14 per cent, respectively. In 1.25 per cent C alloys and at similar manganese concentrations the Q values are 61,200 and $61,000 \pm 1000$ cal., respectively.

Q values have been calculated also from the Dushman-Langmuir equation¹⁶ using the diffusion data of Fig. 5 (lower curve) and of test 15, and the results are given in Fig. 7. These are in agreement with the Q values referred to above within the limits of experimental error. In applying the Dushman-Langmuir equation the "diffusion-jump distance," δ , was taken as equal

to $a_0 \frac{\sqrt{2}}{2}$ where a_0 is the side of the unit cell; the a_0 value was taken from the work of Walters and co-authors^{10,11} and from that of Esser and Müller.¹²

Although this equation appears to be in disrepute among physicists at the moment, it furnishes Q values in good agreement

few data are available for a graphical determination of Q . The Q values given for percentages of manganese above 20 were obtained in this way.

From the values of D at various temperatures and concentrations and those of Q at various concentrations, values of A have been calculated. As previously shown⁵ the experimental error in Q has a much greater effect than that of D on the error in A . For this reason two values of A were calculated for each set of concentrations, one assuming the highest probable value of Q and the other the lowest value. The difference between the two values of A obtained were assumed to cover the probable error range.

The A values for iron-manganese alloys (less than 0.02 per cent C) were found to be 0.57 ± 0.11 and 0.54 ± 0.09 sq. cm. per sec. at 4 and 14 per cent Mn, respectively, and for the high-carbon ternary alloys (1.25 per cent C) to be 0.51 ± 0.18 and 0.52 ± 0.18 sq. cm. per sec. at similar

manganese concentrations. Within the limit of experimental error, A apparently is constant irrespective of manganese or carbon concentration up to 14 per cent Mn and 1.25 per cent C.

The Diffusion Equation.—For each of the four concentrations designated below, specific value may now be written into the general diffusion equation, $D = A \times e^{-\frac{Q}{RT}}$

Mn 4%, C 0.02%:

$$D_{\text{Mn}}^{\gamma\text{Fe}} = (0.57 \pm 0.11)e^{-\frac{66,200 \pm 500}{RT}} \quad [1]$$

Mn 14%, C 0.02%:

$$D_{\text{Mn}}^{\gamma\text{Fe}} = (0.54 \pm 0.09)e^{-\frac{65,400 \pm 500}{RT}} \quad [2]$$

Mn 4%, C 1.25%:

$$D_{\text{Mn}}^{\gamma\text{Fe}} = (0.51 \pm 0.18)e^{-\frac{61,200 \pm 1000}{RT}} \quad [3]$$

Mn 14%, C 1.25%:

$$D_{\text{Mn}}^{\gamma\text{Fe}} = (0.52 \pm 0.18)e^{-\frac{61,000 \pm 1000}{RT}} \quad [4]$$

An empirical equation may be derived, which can be used to calculate diffusion coefficient values in iron-manganese alloys with an accuracy of ± 15 per cent, over a temperature of about 500°C. (950° to 1450°C.) and over a composition range of from close to zero to at least 20 per cent Mn and probably to 60 per cent Mn:

$$D_{\text{Mn}}^{\gamma\text{Fe}} = (0.486 + 0.011 \times \text{Wt. \% Mn})e^{-\frac{66,000}{RT}} \quad [5]$$

A similar equation may be derived to calculate the rate of diffusion of manganese at carbon concentration between 0.0 and 1.5 per cent C, when the D value at one carbon concentration is known.

$$D_{C_x} = D_{C_0}(1 + 2.53 \times \text{Wt. \% C}) \quad [6]$$

where D_{C_0} is the D value at 0 per cent C and D_{C_x} is the D value at concentration C_x .

DISCUSSION OF RESULTS

The values of D given in the foregoing paragraphs for manganese in γ -Fe are only $\frac{1}{300}$ of that calculated by Clausen⁴ from

Fry's data.² Fry's data are scanty. He diffused manganese from Goldschmidt's manganese through the vapor phase into specimens of electrolytic iron. A calculation of D from other data of Fry furnishes a value only five times too high; his data are thus widely variable and his experimental procedure must not have been under close control.

Paschke and Hauttmann³ believe their results to have been vitiated by loss of manganese during the diffusion anneal. The values of D given above are about $\frac{1}{80}$ of those given by these workers. Their experiment suffered not only from loss of manganese but probably also from gain of manganese in the low-manganese ends of the diffusion specimens. It has been noted above that neither of the previous investigations took account of the variation of D with concentration, though this in itself does not account for the wide divergence in the data.

It has been pointed out^{1,13} that the effect of alloying elements, such as manganese and nickel, upon the hardenability of steels on quenching lies in their effect in retarding the rate of formation of pearlite from austenite, and that this effect originates in a reduced rate both of nucleation (N) and of growth (G) of the pearlite nodules. Little can be said at the moment concerning the effect of alloying elements upon N , but their effect upon G is clearer. The formation of pearlite is a process of segregation, in which carbon segregates preferentially to the cementite and in which the alloying element segregates preferentially either to the cementite or to the ferrite, according to whether the alloying element is or is not a carbide-forming element. We now see, on the basis of the results given here and those given earlier,⁵ that at 1000°C. manganese diffuses at a rate roughly $\frac{1}{50,000}$ of that of carbon. By extrapolation it is found that at 700°C., a temperature at which pearlite actually forms, manganese diffuses in the austenite in the composition range 0.6 to

0.9 per cent C, 0.1 to 4 per cent Mn at a rate of about $1/3,000,000$ of that of carbon. Manganese is, therefore, a much less mobile atom and accordingly greatly retards the rate of growth of the pearlite nodule; the effect of manganese in reducing the rate of nucleation may be merely one of decreasing the probability of the occurrence of the original pearlite nucleus.¹³ A more complete analysis of this problem will require a more thorough knowledge of the effect of alloying elements upon the interlamellar distance, better ideas concerning the effective concentration gradients at the pearlite-austenite interface, and additional and better information concerning the partition of alloying element between carbide and ferrite.

Because of the high mobility of the carbon atom and the low mobility of the manganese atom, steels containing iron, manganese and carbon are much more readily homogenized with respect to carbon than to manganese. A steel in the composition range 0.1 to 0.5 per cent C, 0.1 to 4 per cent Mn, which could be homogenized with respect to carbon in $\frac{1}{2}$ hr. at 1000°C . would require about 100 hr. at 1400°C . to homogenize it with respect to manganese, assuming the degree of heterogeneity to be the same for carbon and manganese prior to the homogenizing heat-treatment (taking the diffusivity coefficient of carbon at 1000°C . as 300×10^{-9} sq. cm. per sec. and that of manganese as 1.5×10^{-9} sq. cm. per sec. at 1400°C .).

Simultaneously with the increase in the rate of diffusion of manganese with increased manganese and carbon, there is a lowering of the melting range and an increase in the size of the unit cell, both of which may be contributory to the increased rates of diffusion observed.¹

SUMMARY

1. Rates of diffusion of manganese in γ -Fe in low-carbon and in high-carbon steels have been determined over a temper-

ature range from 1050° to 1450°C . and from 1000° to 1250°C ., respectively, and at compositions between 4 and 60 per cent Mn and between 0.02 and 1.25 per cent C. These data are accurate within ± 15 per cent.

2. Q , the activation heat of diffusion, has been calculated at various manganese concentrations. At 4 per cent Mn and 0.02 per cent C, Q is $66,200 \pm 500$ cal. per gram-atomic weight; at 14 per cent Mn and 0.02 per cent C, at 4 per cent Mn and 1.25 per cent C, and at 14 per cent Mn, 1.25 per cent C, the values are 65,400 cal., 61,200 cal. and 61,000 cal. per gram-atomic weight, respectively. These values may also be calculated from the Dushman-Langmuir equation.

3. The rate of diffusion of manganese increases by about 125 per cent as the composition changes from close to zero to 60 per cent Mn, and by about 350 per cent as the carbon is increased from 0 to 1.5 per cent. This percentage change of D with manganese or carbon content is roughly independent of temperature.

4. Impurities normally present in commercial steels do not affect the rate of diffusion of manganese appreciably. The high silicon content of Hadfield steels, 0.3 to 1.0 per cent, changes the rate of diffusion of manganese only slightly, if at all.

5. Diffusion equations at manganese concentrations of 4 and 14 per cent and at carbon concentrations of 0.02 and 1.25 per cent, are:

Mn 4%, C 0.02%:

$$D_{\text{Mn}}^{\gamma\text{Fe}} = (0.57 \pm 0.11)e^{-\frac{66,200 \pm 500}{RT}} \quad [1]$$

Mn 14%, C 0.02%:

$$D_{\text{Mn}}^{\gamma\text{Fe}} = (0.54 \pm 0.09)e^{-\frac{65,400 \pm 500}{RT}} \quad [2]$$

Mn 4%, C 1.25%:

$$D_{\text{Mn}}^{\gamma\text{Fe}} = (0.51 \pm 0.18)e^{-\frac{61,200 \pm 1000}{RT}} \quad [3]$$

Mn 14%, C 1.25%:

$$D_{\text{Mn}}^{\gamma\text{Fe}} = (0.54 \pm 0.18)e^{-\frac{61,000 \pm 1000}{RT}} \quad [4]$$

6. An empirical equation is provided from which D values at manganese concentrations between 0 and 20 per cent may be calculated in iron-manganese alloys within 15 per cent:

$$D_{\text{Mn}}^{\gamma\text{Fe}} = (0.486 + 0.011 \times \text{Wt. \% Mn}) e^{-\frac{66,000}{RT}} \quad [5]$$

A similar equation is provided from which D values can be calculated within ± 20 per cent at any carbon concentration between 0 and 1.5 per cent when the value at one carbon concentration is known:

$$D_{C_x} = D_{C_0}(1 + 2.53 \times \text{Wt. \% C}) \quad [6]$$

where D_{C_0} is the D value at 0 per cent C and D_{C_x} is the D value at concentration C_x .

7. Microscopic evidence is given, which shows, although not conclusively, that grain size does not greatly affect the rate of diffusion of manganese in γ -Fe.

ACKNOWLEDGMENTS

The authors are grateful to their friends in the steel industry and in the International Nickel Co. for their ready cooperation in furnishing numerous chemical analyses and in supplying materials. They also appreciate the assistance given by Miss E. B. Pearsall and other members of the staff of the Metals Research Laboratory.

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DISCUSSION

(Eric R. Jette presiding)

R. W. GURRY,* Kearny, N. J.—In considering the effect of manganese on the rate of growth of pearlite nuclei, it should be remembered that this growth is more rapid when manganese is absent, and, accordingly, the presence of manganese is not required for the carbide to form. Consequently, the reduced rate of growth in a manganese steel would appear to be caused not by the slow diffusion of the manganese directly but rather by the effect of manganese in decreasing the rate of diffusion of carbon. The manganese would then concentrate in the carbide phase simply because it found time to do so.

However, the presence of manganese has been shown to increase the rate of carbon diffusion⁵ in austenite. How can this fact be reconciled with the statement that the rate of growth of pearlite nuclei is reduced by the presence of manganese in view of the above discussion?

In applying the Dushman-Langmuir equation the authors in a previous paper⁵ took as the "diffusion-jump distance," δ , for carbon in austenite, $\frac{1}{2}$ of the edge length of the unit cube; in the present paper δ is assumed to be $\frac{\sqrt{2}}{2}$ times the cube-edge length, the difference supposedly being due to the fact that in the case of carbon dissolved in austenite the solution is

* Research Laboratory, U. S. Steel Corporation.

of the interstitial type while for manganese it is of the substitutional type. However, the shortest jump for a carbon atom situated in the center of a unit face-centered cube of austenite is to the middle of one of the edges, which position is in reality the center of another unit cube. The distance of this jump is $\frac{\sqrt{2}}{2}$ times the cube-edge length, and δ would appear to be calculated in the same manner independent of the type of solution.

M. A. BREDIG,* New York, N. Y.—I should like to ask whether the middle of the edges in this face-centered lattice can be considered equivalent for placement of carbon, and therefore its jumping distance also equal to half the face diagonal?

C. WELLS AND R. F. MEHL (authors' reply).—Mr. Gurry's question is the basic one in the theory of the effect of alloying elements on the rate of formation of pearlite. The problem is by no means simple and though we have discussed it in a number of places^{1,13} we regard our opinion as tentative.

Manganese has a negligible effect upon the interlamellar spacing of pearlite; the effect of manganese upon the rate of formation of

pearlite is therefore not structural and must be sought in purely kinetic factors. Since we have shown that manganese does not decrease the rate of diffusion of carbon in austenite, we have maintained that the rate of formation of pearlite is decreased by manganese because of the requirement that manganese must diffuse and because it diffuses more slowly than carbon. Whether manganese decreases the rate of reaction at the austenite-pearlite interface, so that this factor, ordinarily not a rate-controlling factor in such reactions, becomes the dominant rate-controlling factor, cannot be said.

We are inclined to agree with Mr. Gurry as to the operative jump distances. Calculations indicate that a considerable change can be made in the assumed value of δ without changing the value of Q calculated from the Dushman equation beyond those limits of error usually associated with Q . For example, at 1 per cent carbon the calculated Q value is 33,500 and 32,000 cal. when δ is assumed to be equal to $\frac{\sqrt{2}}{2} a_0$ and $\frac{a_0}{2}$, respectively. The best value of δ now available is $32,000 \pm 1,000$ calories.

These comments will serve also in answer to Mr. Bredig's question.

[For further discussion of this paper,
see page 338]

* Manager, Applied Chemicals Division, Vanadium Corporation of America.

Rate of Diffusion of Nickel in Gamma Iron in Low-carbon and High-carbon Nickel Steels

BY CYRIL WELLS* AND ROBERT F. MEHL,† MEMBERS A.I.M.E.

(New York Meeting, February 1941)

THE two earlier papers in this series^{1,2} presented data on the rate of diffusion of carbon and of manganese in gamma iron. Apart from their scientific interest, these purities, and of grain size on these rates have been studied.) Claussen,³ using the data of Fry,⁴ has calculated the diffusion coefficient of nickel

TABLE I.—Composition of Alloys

Alloy No.	Composition, Weight Per Cent							
	Ni	C	Si	Mn	P	S	Cu	O ₂
1A	1.9	0.05	0.11	0.28	0.01	0.02	0.08	
2A	20.1	0.06	0.12	0.28	0.009	0.020	0.100	
2B	20.1	0.06	0.12	0.28	0.009	0.020	0.100	
3A	1.9	0.60	0.27	0.56	0.027	0.025	0.078	
4B	19.8	0.60	0.26	0.52	0.025	0.017	0.060	
5B ^a	25.0	0.02	0.01	<0.005	<0.005	<0.005	0.05	0.003
6A	0.0	0.02	<0.005	<0.005	<0.005	<0.005	0.036	0.003
7A	1.7	0.27	0.21	0.45	0.014	0.025	0.082	
8B	19.7	0.28	0.27	0.54	0.020	0.020	0.080	
9A	8.0	0.02	0.11	0.18	0.01	0.02		
10A	41.8	0.02	0.08	0.17	0.006	0.023		
10B	41.8	0.02	0.08	0.17	0.006	0.023		
11A	59.7	0.03	0.05	0.17	0.003	0.021		
11B	59.7	0.03	0.05	0.17	0.003	0.021		
12A	79.3	0.01	0.05	0.20	0.002	0.016		
12B	79.3	0.01	0.05	0.20	0.002	0.016		
13B ^b	99.4	0.001	0.11	0.37	0.02	0.02		
14A	0.0	1.10	0.070	0.40	0.017	0.036		
15B	8.0	1.35	0.25	0.50	0.025	0.022		
16A	0.0	0.006	0.005	0.008	0.006	0.020	0.040	0.19

^a Alloy 5B contains 0.12 per cent Co and spectroscopic traces of molybdenum and chromium.

^b Alloy 13B contains 0.10 per cent magnesium.

data are needed chiefly in order to treat data on carburization, on rate of formation of pearlite, and on rate of austenitizing in a quantitative way.^{1,2,9,10} In the present investigation rates of diffusion of nickel in γ -Fe over wide temperature and concentration ranges have been determined, and the effects of carbon, of im-

in γ -Fe as 9.2×10^{-11} sq. cm. per sec. at 1200°C., but had no data from which to calculate the variation of D with concentration, temperature, and percentage of carbon.

METHOD AND MATERIALS

Method.—Nickel was diffused along the axis of a cylindrical specimen across a concentration gradient, concentration-penetration curves were determined and D values calculated from Grube or Matano solutions.⁵ Details of the method are given

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¹ References are at the end of the paper.

TABLE 2.—*Heat-treatment and Grain-size Data*

Test No.	Alloys Welded ^a	Temperature of Diffusion, Deg. C.	Time of Diffusion, Hr.	Carbon Content, Wt. Per Cent			Average Number of Austenite Grains per Sq. Mm.	
				Range before Test	After Test	Assumed Average	Alloy A	Alloy B
1	3A- 4B	1050	1500	0.60-0.60	0.66	0.63	8	8
2	1A- 2B	1100	1000	0.05-0.06	0.04	0.05	4 ^b	8
3	1A- 2B	1100	1000	0.05-0.06	0.20	0.13	4 ^b	4
4	3A- 4B	1100	1000	0.60-0.60	0.40	0.50	8	4
5	1A- 2B	1158	1000	0.05-0.06	0.28	0.17	4 ^b	4
6	3A- 4B	1158	1000	0.60-0.60	0.26	0.43	4	4
7	1A- 2B	1205	433	0.05-0.06	0.17	0.11	1 ^b	8
8	1A- 2B	1205	1000	0.05-0.06	0.26	0.16	2 ^b	2
9	3A- 4B	1205	433	0.60-0.60	0.44	0.52	4	4
10	3A- 4B	1205	1000	0.60-0.60	0.38	0.49	2	2
11	1A- 2B	1260	300	0.05-0.06	0.18	0.12	4 ^b	4
12	3A- 4B	1260	174	0.60-0.60	0.45	0.53	16	16
13	6A- 5B	1300	127	0.02-0.02	0.02	0.02	1 ^b	16
14	1A- 2B	1300	275	0.05-0.06	0.02	0.03	8 ^b	
15	16A- 5B	1300	193	0.01-0.02	0.01	0.01	<1 ^b	9
16	6A- 2B	1300	240	0.02-0.06	0.03	0.03	<1 ^b	16
17	6A- 2B	1300	243	0.02-0.06	0.02	0.03	<1 ^b	4
18	2A-10B	1300	240	0.06-0.02	0.03	0.03		8
19	12A-13B	1300	240	0.01-0.01	0.01	0.01	<1	<1
20	6A-13B	1300	240	0.02-0.01	0.01	0.01	4 ^b	1
21	3A- 4B	1300	268	0.60-0.60	0.63	0.61	<1	<1
22	14A-15B	1250	193	1.35-1.10	1.23	1.23	1	<1
23	1A- 2B	1340	192	0.05-0.06	0.02	0.03	<1	<1
24	1A- 2B	1390	176.5	0.05-0.06	0.02	0.03	<1	<1
25	1A- 2B	1300	240	0.05-0.06	0.10	0.07	64 ^b	1
26	9A- 2B	1450	60	0.02-0.06	0.02	0.03	4	<1

^a Analysis of alloys given in Table 1.^b These are ferrite grain sizes.

Table 3. See footnote on page 317.

TABLE 4.—*Diffusion Data, Nickel in Gamma Iron*

Test No.	Nickel Range in Specimen, Wt. Per Cent	Temperature of Diffusion, Deg. C.	Carbon Content ^a	$D \times 10^{11}$ Sq. Cm. per Sec. at Various Nickel Concentrations, Atomic Per Cent ^{b,c,e}					
				4 %	16 %	30 %	50 %	70 %	90 %
1	1.9-19.8	1050	0.63	0.79	1.02				
2	1.9-20.1	1100	0.05	0.88	1.1				
3	1.9-20.1	1100	0.13	0.95	1.1				
4	1.9-19.8	1100	0.50	1.5	1.7				
5	1.9-20.1	1158	0.17	2.7	3.4				
6	1.9-19.8	1158	0.43	3.2	3.8				
7	1.9-20.1	1205	0.11	4.1	5.2				
8	1.9-20.1	1205	0.16	4.9	5.9				
9	1.9-19.8	1205	0.52	7.7	10.0				
10	1.9-19.8	1205	0.49	7.0	8.2				
11	1.9-20.1	1260	0.12	11	17				
12	1.9-19.8	1260	0.53	19	24				
13	0.0-25.0	1300	0.02	17	29				
14	1.9-20.1	1300	0.03	17	29				
15	0.0-25.0	1300	0.01	18	24				
16 ^d	0.0-20.1	1300	0.03	15	20				
17	0.0-20.1	1300	0.03	15	20				
18	20.1-41.8	1300	0.03			47			
19	79.3-99.4	1300	0.01			(59)	(108)	(193)	193 (183)
20	0.0-99.4	1300	0.01						
21	1.9-19.8	1300	0.61	34	46				
22	0.0- 8.0	1250	1.23	(35)					
23	1.9-20.1	1340	0.03	29	41				
24	1.9-20.1	1390	0.03	57	63				
25	1.9-20.1	1300	0.07	16	23				
26	8.0-20.1	1450	0.03		160				

^a These data are taken from Table 2, column 7.^b Equivalent weight per cent values are higher, but the difference is insignificant.^c The Matano method was used to calculate all D values in parentheses and the Grube method to calculate other values.^d Specimen 16, test 16, was heated in hydrogen. All other specimens were heated in argon.^e In the calculation of D values, account was taken of the fact that the concentration gradients across the diffusion zones at diffusion temperatures and room temperatures respectively are different.

in an earlier paper.¹ All specimens were heated in argon, except in one test in which the specimen was heated in hydrogen.

given in Table 1. Some of the materials listed were relatively pure, while others were of commercial grade.

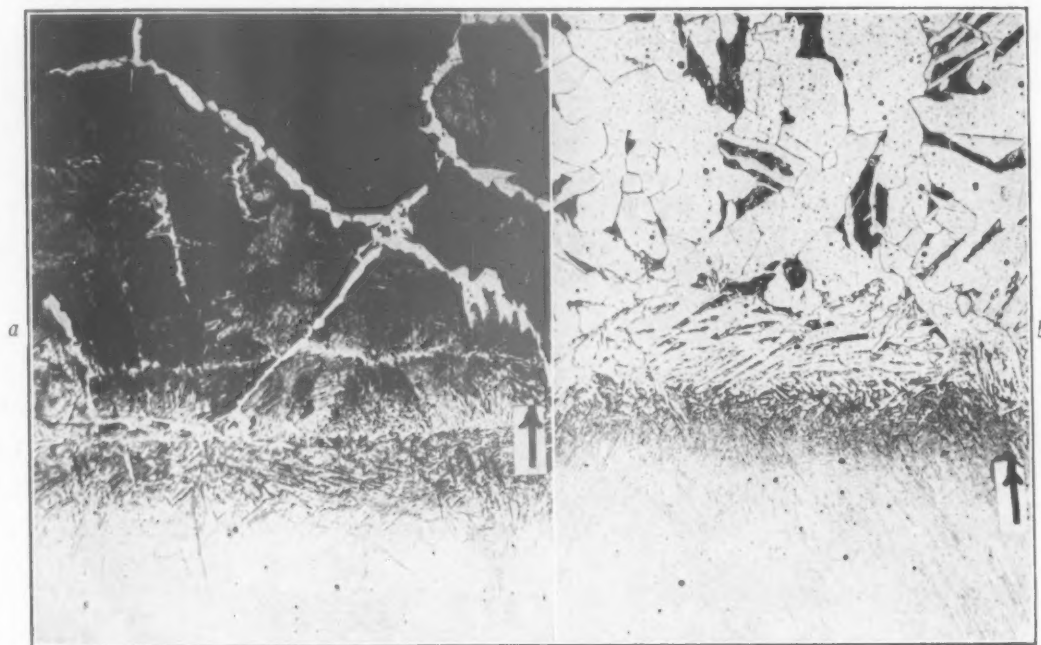


FIG. 1.—TYPICAL MICROSTRUCTURES. $\times 100$.

a, alloys with 19.8 per cent Ni, 0.6 per cent C (lower) and 1.9 per cent Ni, 0.6 per cent C (upper) were welded. The specimen was subsequently heated at 1050°C. for 1500 hours and cooled at 2° per minute.

b, alloys with 20.1 per cent Ni, 0.05 per cent C (lower) and 1.9 per cent Ni, 0.05 per cent C (upper) were welded. The specimen was subsequently heated at 1205°C. for 433 hours and cooled at 2° per minute.

Arrows indicate positions of welds.

Temperatures are accurate within 3°C. and constant within 1°C.; times are accurate to within $\frac{1}{2}$ hr. Specimens were furnace-cooled from diffusion-anneal temperatures at about 2° per minute. Layers about 0.004 in. thick and parallel to the welded interface were machined from the specimen after the diffusion-anneal and analyzed for nickel to 0.1 per cent; the distances of these layers from the interface were measured to ± 0.0002 in. For calculating D values the Grube solution was used in all cases except where the effect of concentration on D was greater than 50 per cent over the concentration range in the specimen, in which case the Matano method was used.

Materials.—The compositions of the iron and iron-nickel-carbon alloys used are

RESULTS

Typical microstructures across diffusion zones after diffusion-annealing are shown in Fig. 1. D values at various temperatures and concentrations are given in Table 4. Original experimental data used in the determination of the values are listed in Table 3.*

Accuracy.—The diffusivity coefficients listed in Table 4 are believed to be correct to within ± 20 per cent. Factors affecting the accuracy of these values have already

* Table 3 has been issued through auxiliary publication and may be obtained from the American Documentation Institute, care Science Service, 2101 Constitution Avenue, Washington, D. C., by ordering Document No. 1463, remitting 25¢ for copy in microfilm (read enlarged to full size on reading machines now widely available), or 70¢ for copy in paper photo-prints legible without mechanical aid.

been discussed in detail.¹ Good reproducibility as shown by check tests (compare test 16 with 17 (Table 4), test 2 with 3, and test 9 with 10 (Table 5)), and by the

tration on the rate of diffusion of nickel is shown in Fig. 3 and the effect of carbon on the rate of diffusion of nickel in Figs. 3 and 4. D increases with nickel concentra-

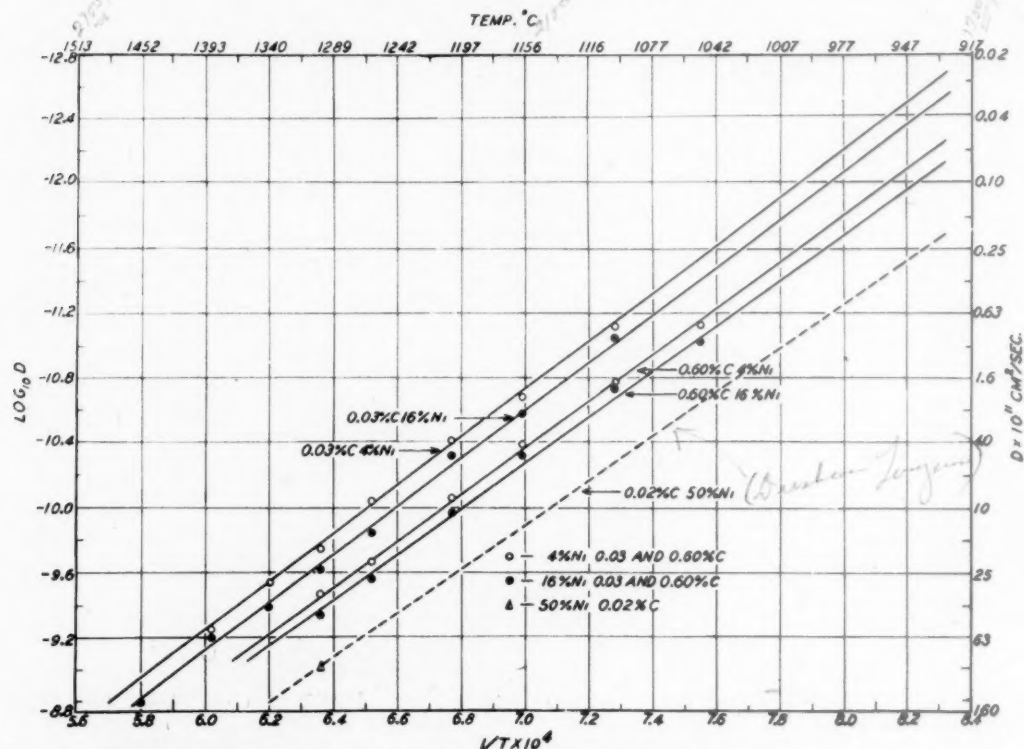


FIG. 2.—PLOT OF $\log_{10} D$ VERSUS $1/T$ (T IN ABSOLUTE DEGREES), AT VARIOUS CONCENTRATIONS. D SHOWN ALSO ON RIGHT IN SQUARE CENTIMETERS PER SECOND, AND TEMPERATURE SHOWN ALSO AT TOP IN DEGREES CENTIGRADE.

consistency of the data as a whole (see Fig. 2) gives assurance of an accuracy greater than usually obtained in a determination of diffusivity coefficients. In test 17 the high-nickel alloy of specimen 17 was heated at 1400°C . for about 175 hr. prior to welding to the low-nickel alloy, and the effect of this preliminary homogenizing treatment on the results obtained was found to be negligible. (Compare results of tests 17 with those of test 14.) While this long heat-treatment may be inadequate to give complete homogenization in the high-nickel alloy, any residual heterogeneity could not have affected the accuracy of the results within the limits stated.

Effect of Concentration of Nickel and of Carbon on D .—The effect of nickel concen-

tion, at first slowly and then more rapidly, and the rate of diffusion is further increased by carbon. Increasing the nickel from close to zero to almost 100 per cent raises the D value from 15 to about 250×10^{-11} sq. cm. per sec. In both the higher and lower carbon ternary alloys (0.03 and 0.6 per cent C, respectively), D is increased by about 80 per cent as the nickel content is raised from close to zero to 20 per cent Ni, and the percentage change of D with concentration is roughly independent of temperature. Up to about 20 per cent Ni and 1.5 per cent C, the rate of diffusion of nickel increases almost linearly with nickel (carbon constant—Fig. 3) and with carbon (nickel constant—Fig. 4). As the carbon concentration is raised from 0.03 to 1.5 per

cent, D is increased by more than 300 per cent. It may be observed in Fig. 4 that the relationship between carbon concentration and percentage of increase of D is

The relationship between temperature and rate of diffusion of nickel at nickel concentrations of 4 and 16 per cent and at carbon concentrations of 0.03 and 0.6 per

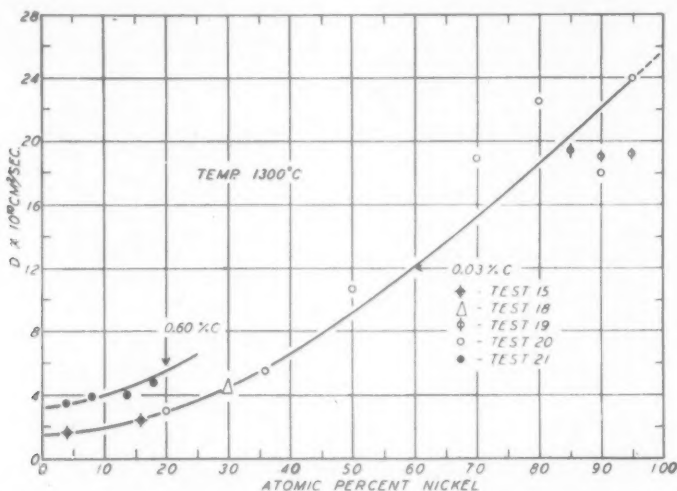


FIG. 3.—RELATIONSHIP BETWEEN DIFFUSIVITY COEFFICIENT AND NICKEL CONCENTRATION AT 0.03 AND 0.6 PER CENT C, RESPECTIVELY.

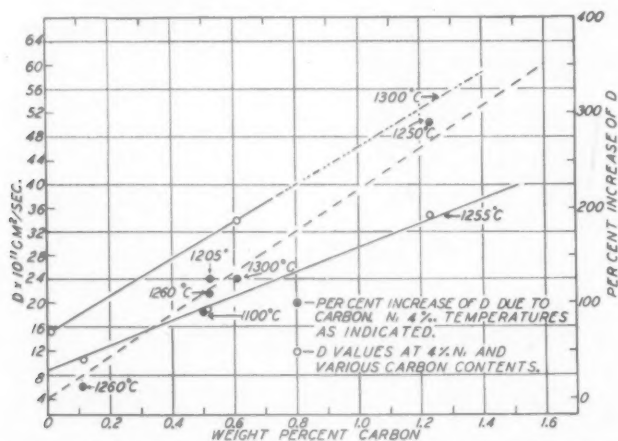


FIG. 4.—CURVES SHOW (1) INCREASE OF D (LEFT-HAND ORDINATE) WITH CARBON CONTENT TO BE ROUGHLY LINEAR (FULL CURVES) AND (2) PER CENT INCREASE OF D (RIGHT-HAND ORDINATE) WITH CARBON CONTENT TO BE APPROXIMATELY INDEPENDENT OF TEMPERATURE (DASHED CURVE).

approximately independent of temperature, at least between 1100° and 1300°C.

Effect of Temperature on D .— D values at 0.03 and 0.6 per cent C, respectively, have been calculated from the relationship between percentage increase of D and carbon content (Fig. 4). The values obtained are listed in Table 5 and those used in the plot of $\log D$ versus $1/T$ (Fig. 2) are referred to in note c of the table.

cent is given in Fig. 2. At the lower carbon concentrations (below 0.03 per cent), the range covered is 350°C. (1100° to 1450°C.) and at higher concentrations the range is 250°C. (1050° to 1300°C.). The dashed line showing the relation between $1/T$ and $\log D$ in a 50 per cent Ni, low-carbon alloy was determined from a known D value at 1300°C. and the Dushman-Langmuir equation.² By using other data from Fig. 3,

the relationship between $\log D$ and $1/T$ at any nickel concentration can be calculated. The accuracy of the dashed line

TABLE 5.—*Diffusion Data, Nickel in Gamma Iron*

AT 4 AND 16 ATOMIC PER CENT NICKEL^a AND AT 0.03 AND 0.6 WEIGHT PER CENT CARBON

Test No.	Temperature, Deg. C.	D × 10 ¹¹ Sq. Cm. per Sec. ^b at 4 Atomic Per Cent Ni and		D × 10 ¹¹ Sq. Cm. per Sec. at 16 Atomic Per Cent Ni and	
		0.03 Per Cent C	0.6 Per Cent C	0.03 Per Cent C	0.6 Per Cent C
1	1050		0.77		0.99
2	1100	0.85		1.06	
3	1100	0.78		0.9	
4	1100		1.7		1.9
5	1158	2.1		2.6	
6	1158		3.9		4.6
7	1205	3.4		4.4	
8	1205	3.9		4.7	
9	1205		8.4		11.0
10	1205		7.9		9.2
11	1260	9.2		14	
12	1260		20		26
13	1300	17		29	
14	1300	17		29	
15	1300	18		24	
16	1300	15		20	
17	1300	15		20	
21	1300		34		46
23	1340	26		41	
24	1390	57		63	
26	1450			160	

^a Equivalent weight per cent values are higher, but the difference is insignificant.

^b The D values are obtained by taking data from Table 4 and by use of equation 6, page 336.

^c Data from tests 1, 3 to 6, 8, 9, 11, 12, 15, 21, 23, 24, and 26 were used in the determination of the $\log D$ versus $1/T$ curves of Fig. 3.

Effect of Impurities.—To determine the effect of oxygen on the rate of diffusion of nickel, D values at 1300°C. were determined in specimens 13 and 15 (see Tables 1 and 2). Except for the oxygen present in specimen 15 (0.19 per cent O₂ at one end) both alloys were of relatively high purity. The D values in tests 13 and 15 at a concentration of 4 per cent Ni, 0.02 per cent C, are identical within experimental error (17 and 18 × 10⁻¹¹ sq. cm. per sec., respectively), showing that this amount of oxygen does not appreciably change the rate of diffusion of nickel in γ -Fe.

Hydrogen has virtually no effect on the rate of diffusion of nickel, as shown by a comparison between the results of tests 16 and 17. Specimen 16 heated in hydrogen and 17 heated in argon gave the same D value, 15 × 10⁻¹¹ sq. cm. per sec., at 1300°C. and at 4 per cent Ni and 0.03 per cent C.

Other impurities, including Mn up to 0.54 per cent, Si up to 0.27 per cent, Cu up to 0.05 per cent, and P and S up to about 0.03 per cent, do not affect the rate of diffusion of nickel appreciably, as is evident from a study of the results of tests 13, 14 and 21. Specimen 13 contains less than 0.005 per cent of each of the elements

TABLE 6.—*Rates of Diffusion*

Temperature, Deg. C.	Rates of Diffusion in Sq. Cm. per Sec. of Nickel in Nickel Steels; Manganese in Manganese Steels, and Carbon in Carbon Steels at Concentrations ^a of				
	4 Per Cent Ni (0.03 Per Cent C)	4 Per Cent Mn (0.03 Per Cent C)	4 Per Cent Ni ^c (0.6 Per Cent C)	4 Per Cent Mn ^c (0.6 Per Cent C)	0.6 Per Cent C ^b
550	4.7 × 10 ⁻¹⁹	15 × 10 ⁻¹⁹	11 × 10 ⁻¹⁹	30 × 10 ⁻¹⁹	3.4 × 10 ⁻¹⁰
720	5.5 × 10 ⁻¹⁶	15 × 10 ⁻¹⁶	13 × 10 ⁻¹⁶	32 × 10 ⁻¹⁶	9.6 × 10 ⁻⁹
1200	3.6 × 10 ⁻¹²	10 × 10 ⁻¹¹	9 × 10 ⁻¹¹	21 × 10 ⁻¹¹	1.9 × 10 ⁻⁶

^a All concentrations are given in weight per cent.

^b The rate of diffusion of carbon in 4 per cent Ni and 4 per cent Mn steels is identical with that in plain carbon steels.¹

^c These are very approximately eutectoid steels.

and others, if similarly determined, obviously depends upon the uncertain validity of this equation, though the results appear reasonable.

mentioned, except for about 0.045 per cent Cu and 0.06 per cent Co; specimen 14 contains about 0.09 per cent Cu, 0.12 per cent Si, 0.28 per cent Mn, 0.005 per cent P

and 0.02 per cent S, and specimen 21 contains about 0.07 per cent Cu, 0.27 per cent Si, 0.54 per cent Mn, 0.026 per cent P, and 0.021 per cent S. At a concentration of 4 per cent Ni and 0.03 per cent C the D values at 1300°C. are 17, 17, and 16* $\times 10^{-11}$ sq. cm. per sec. in tests 13, 14 and 21, respectively.

— *Effect of Grain Size.*—It was not found possible to determine the effect of grain size on the rate of diffusion of nickel, for at useful diffusion anneal temperatures all grains become large, and a distinction between the behavior of small and large grains is impossible. For this reason information relating to the effect of grain size on D must be inferred from the results of microscopic studies.

Typical microstructures are shown in Fig. 1; these appear to show that the "diffusion front" at a given nickel concentration in the diffusion zone cuts the plane of polish to give straight traces irrespective of the presence of grain boundaries. The small irregularities observed are believed to occur as a result of a redistribution of constituents following the transformation on cooling. Apparently grain size has little or no effect on the rate of diffusion of nickel. The circumstances here are thus quite similar to those obtaining in the diffusion of manganese in γ -Fe.²

— *Q and A Values.*— Q values have been calculated at concentrations of 4 and 16 per cent Ni, and at 0.03 and 0.6 per cent C, respectively, from the slopes of the full straight lines in Fig. 2; A values have been calculated from the diffusion equation

$D = A \times e^{-\frac{Q}{RT}}$ when the D and Q values are known.

The Q values at 0.03 per cent and at 4 and 16 per cent Ni are 67,700 and 67,300 ± 750 cal., respectively, and at 0.6 per

cent C and similar nickel concentrations they are 65,500 and 64,500 ± 1000 cal., respectively. These values are in good agreement with comparable values calculated by the use of the Dushman-Langmuir equation*⁶ (Fig. 5).

Since, despite the uncertain validity of the Dushman-Langmuir equation, it appears to provide good agreement with experiment in these studies, it has been employed to calculate Q values at nickel concentrations for which diffusion data are inadequate. Q values calculated in this way at concentrations up to 90 per cent Ni are given in Fig. 5.

Values of A at various compositions have been calculated from the diffusion equation after substituting values of D and Q . The experimental error in Q is greater than in D ¹; for this reason two values of A were calculated at each given concentration, using first the higher and then the lower probable value of Q , and it is assumed that the difference between the two values of A obtained at a chosen concentration gives the probable error range.

In iron-nickel alloys (0.03 per cent C or less) the A values are 0.44 \pm 0.11 and 0.51 \pm 0.12 sq. cm. per sec. at 4 and 16 per cent Ni, and in the ternary alloys containing 0.6 per cent C and 4 and 16 per cent Ni, respectively, the values are 0.46 \pm 0.15 and 0.42 \pm 0.13. These results show that within experimental error A is a constant irrespective of a variation of carbon concentration up to 0.6 per cent and nickel up to 16 per cent.

— *The Diffusion Equation.*—Specific values may now be written into the diffusion

equation $D = A \times e^{-\frac{Q}{RT}}$ as follows:

* This figure is calculated from the D value at 0.61 per cent C, 4 per cent Ni given in Table 4 and the known relationship between D and carbon content (see Fig. 4).

* In applying the Dushman-Langmuir equation, δ is assumed to be equal to $a_0\sqrt{2}/2$ (a_0 = side of unit face-centered cubic cell) and the a_0 data were taken from the work of Jette and Foote⁷ and Lohr and Hopkins.⁸ D values used to calculate Q values were taken from curves of Fig. 3.

Ni 4%, C 0.03%:

$$D_{\text{Ni}}^{\gamma\text{Fe}} = (0.44 \pm 0.11)e^{-\frac{67,700 \pm 750}{RT}} \quad [1]$$

Ni 16%, C 0.03%:

$$D_{\text{Ni}}^{\gamma\text{Fe}} = (0.51 \pm 0.12)e^{-\frac{67,300 \pm 750}{RT}} \quad [2]$$

where D_{c_0} is the D value at 0 per cent C and D_{c_x} is the D value at concentration c_x .

DISCUSSION OF RESULTS

Claussen's³ calculation of the diffusivity coefficient of nickel in γ -Fe at 1200°C.,

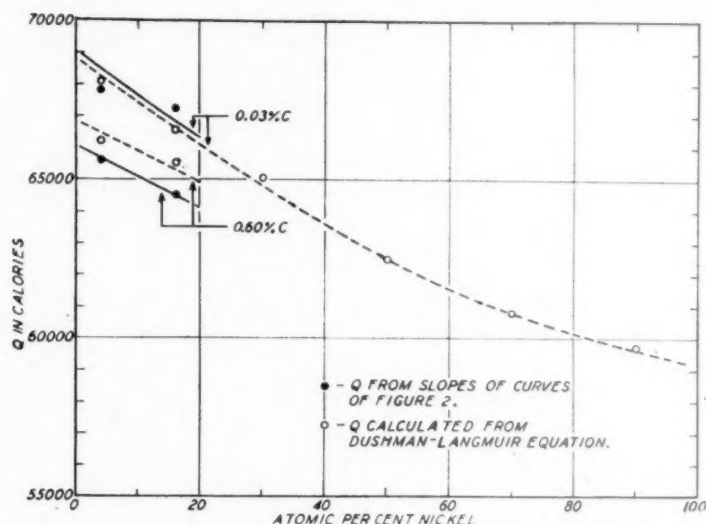


FIG. 5.—RELATIONSHIP BETWEEN Q (IN CALORIES PER GRAM ATOM) AND NICKEL CONCENTRATION AT 0.03 AND 0.6 PER CENT C, RESPECTIVELY.

Ni 4%, C 0.6%:

$$D_{\text{Ni}}^{\gamma\text{Fe}} = (0.46 \pm 0.15)e^{-\frac{65,500 \pm 1000}{RT}} \quad [3]$$

Ni 16%, C 0.6%:

$$D_{\text{Ni}}^{\gamma\text{Fe}} = (0.42 \pm 0.13)e^{-\frac{64,500 \pm 1000}{RT}} \quad [4]$$

An empirical equation may be written from which diffusion coefficients in iron-nickel alloys up to about 20 per cent Ni can be calculated with an accuracy of ± 20 per cent over a temperature range of about 500°C. (950° to 1450°C.):

$$D_{\text{Ni}}^{\gamma\text{Fe}} = (0.344 + 0.012 \times \text{Wt \% Ni})e^{-\frac{67,500}{RT}} \quad [5]$$

Given a D value at one carbon concentration, values at other concentrations can be calculated with an accuracy of about 20 per cent over a range of 0 to 1.5 per cent C from the following equation:

$$D_{c_x} = D_{c_0}(1 + 2.3 \text{ Wt \% C}) \quad [6]$$

9.2×10^{-11} sq. cm. per sec., was made without regard to the effect of concentration on D . The present results show the D value to increase many times as the nickel content is raised from 0 to 100 per cent Ni, and Claussen's figure, which happens to be correct at a concentration of about 25 per cent Ni, is in considerable error at others.

It is apparent from the tabulated D values (Table 6) that manganese in steels diffuses faster than nickel, and carbon much faster than either. In view of this it would be expected that nickel and manganese would decrease the rate of nucleation and the rate of growth of pearlite nodules in the austenite-pearlite reaction observed. As shown earlier,¹⁰ however, a full quantitative analysis of the rate of formation of pearlite will require information on other factors.

Relative rates of homogenization in manganese, nickel and carbon steels can

be computed, using the data given in Table 6. Assuming a like degree of heterogeneity, a eutectoid manganese steel should be homogenized at 1200°C. in about one-half the time for a eutectoid nickel steel; the time required to homogenize both manganese and nickel steels with respect to carbon should be relatively insignificant.

The rate of diffusion of nickel increases with concentration up to almost 100 per cent Ni and simultaneously the melting temperatures are at first decreased and then increased (minimum at 60 per cent Ni); the size of the unit cell is at first increased and then decreased (maximum at 40 per cent Ni). Apparently there seems to be no close correlation in the gamma range of the iron-nickel system between the rate of diffusion and either the melting range⁹ or the size of the unit cell. The data show also that the difference in the carbide-forming tendencies of nickel and manganese is in no way anticipated in the gamma solid solution.

SUMMARY

1. Diffusion rates of nickel in γ -Fe have been determined with an accuracy of ± 20 per cent between 1050° to 1450°C., at compositions between 0 and 100 per cent Ni, and between 0.01 and 1.23 per cent C.

2. Values of the activation energy, Q , have been determined graphically from these data at concentrations of 4 and 16 per cent Ni in nickel steels containing 0.03 and 0.6 per cent C, respectively. Values at higher nickel concentrations have been calculated by the Dushman-Langmuir equation.

3. The rate of diffusion of nickel is increased by several orders of magnitude as the nickel content is increased from close to zero to nearly 100 per cent Ni. Over a range from 0 to 20 per cent Ni, D increases by about 80 per cent. At constant nickel concentration, D increases by more than 300 per cent as the carbon content is raised from 0 to 1.5 per cent. The percent-

age change of D with manganese and carbon content is roughly independent of temperature.

4. Impurities in amounts usually present in commercial steels have no appreciable effect on the rate of diffusion of nickel.

5. Diffusion equations at nickel concentrations of 4 and 16 per cent and at carbon concentrations of 0.03 and 0.6 per cent are:

(a) Ni 4%, C 0.03%:

$$D_{\text{Ni}}^{\gamma\text{Fe}} = (0.44 \pm 0.11)e^{-\frac{67,700 \pm 750}{RT}}$$

(b) Ni 14%, C 0.03%:

$$D_{\text{Ni}}^{\gamma\text{Fe}} = (0.51 \pm 0.12)e^{-\frac{67,300 \pm 750}{RT}}$$

(c) Ni 4%, C 0.6%:

$$D_{\text{Ni}}^{\gamma\text{Fe}} = (0.46 \pm 0.15)e^{-\frac{65,500 \pm 1000}{RT}}$$

(d) Ni 14%, C 0.6%:

$$D_{\text{Ni}}^{\gamma\text{Fe}} = (0.42 \pm 0.13)e^{-\frac{64,500 \pm 1000}{RT}}$$

6. An empirical equation is given from which D values at nickel concentrations between 0 and 20 per cent may be calculated within ± 20 per cent in iron-nickel alloys:

(e) $D_{\text{Ni}}^{\gamma\text{Fe}}$

$$= (0.344 + 0.012 \times \text{Wt \% Ni})e^{-\frac{67500}{RT}}$$

A similar equation is provided from which D may be calculated at C concentrations between 0 and 1.5 per cent within ± 20 per cent when a value at one concentration is known, as follows:

$$D_{C_x} = D_{C_0}(1 + 2.3 \text{ Wt \% C})$$

where D_{C_0} is the diffusivity value at 0 per cent C and D_{C_x} is the value at concentration C_x .

7. Microscopic studies show, though not conclusively, that grain size has little or no effect on the rate of diffusion of nickel in γ -Fe.

ACKNOWLEDGMENTS

The authors are indebted for friendly assistance from the steel industry and the

International Nickel Co. in supplying materials and making numerous chemical analyses. They also wish to thank Miss E. B. Pearsall for her assistance in the experimental work.

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DISCUSSION

(Eric R. Jette presiding)

[This discussion refers also to the paper that begins on page 315]

J. B. AUSTIN,* Kearny, N. J.—In every science there are a number of fundamental data, which form the basis for many calculations, and which need, therefore, to be determined accurately. Unfortunately, the precise measurement of these quantities is almost always slow, requires painstaking and careful work, and offers little chance of obtaining spectacular results, so that it is not as attractive as certain other investigations. It is true that occasionally, as in Milliken's determination of the charge on the electron, the value of the result is widely recognized and the investigator is suitably rewarded, but in general the accumulation of these precise data is routine work, which never finds the front page. When, therefore, we find investigators devoting themselves

to the type of work described in these papers, which is a very valuable contribution to the fundamental data on diffusion in iron, it is fitting that we express to them our appreciation of their efforts.

I should like to ask the authors their opinion about the composition of the carbides that appear in manganese steels such as those used in their work. It has seemed to me that we have been too ready to accept the conclusion that carbides appearing in iron have a fairly constant composition. It seems only reasonable that they should show a variation in composition and I should like to know whether the authors have obtained any evidence bearing on this matter.

C. WELLS AND R. F. MEHL (authors' reply). As Dr. Austin has spent considerable time in making quantitative measurements of value in the development of metallurgy, he appreciates not only the importance of such work but also some of the difficulties. While it is true that such work does not attract wide attention, for it is not spectacular, it is true also that sound development of the science of physical metallurgy will increasingly require careful quantitative measurements so that the science itself may approach a more quantitative stage.

As to the compositions of the carbides: Manganese atoms may replace about one quarter of the iron atoms in cementite, without appreciably changing the size of the unit cell of cementite.^{1,3} Carbides separated from alloys of about 1 per cent C and 5 to 13 per cent Mn were found by Arnold and Read² to contain about 22 per cent Mn and 7 per cent C (difference iron), and in an alloy with 1 per cent C and only 0.5 per cent Mn, the manganese content of the carbide was found to be between 2 and 3 per cent. In ternary alloys containing more than 22 per cent Mn, other carbides may exist. Westgren and Phragmén³⁻⁵ have reported the

¹ J. L. Holmquist: The Constitution of Iron-manganese-carbide occurring in Iron-manganese-carbon alloys. Thesis (M.S.) Carnegie Inst. of Technology, 1931. (Carnegie Library, Pittsburgh.)

² J. O. Arnold and A. A. Read: The Chemical and Mechanical Relations of Iron, Manganese, and Carbon Alloys. *Jnl. Iron and Steel Inst.* (1910) **81**, 169.

³ A. Westgren and G. Phragmén: X-ray Studies on the Crystal Structure of Steel. *Jnl. Iron and Steel Inst.* (1922) **105**, 241.

⁴ A. Westgren and G. Phragmén: *Kungl. Svenska Vetenskapsakademiens Handlingar* (1926) **2**.

⁵ A. Westgren and G. Phragmén: X-ray Studies on the Crystal Structure of Steel, pt. 2. *Jnl. Iron and Steel Inst.* (1924) **109**, 159.

* Research Laboratory, United States Steel Corporation.

presence of Mn_4C (or Mn_{23}C_6) and Mn_7C_3 ; in steels very high in manganese, they state that some manganese may be replaced by iron, giving $(\text{MnFe})_4\text{C}$ or $(\text{MnFe})_7\text{C}_3$.

We have recently reviewed the literature on the composition of alloy carbides. The data are simply not very good, and the whole field is one that should be restudied with more precise methods. What these methods should be is hard to say, for it appears that new methods must be developed if improved results are to be obtained. It is, however, a problem of great importance in the understanding of the behavior of alloy steels, and it is a problem to which an analytical chemist could well turn his attention. We agree with Dr. Austin that it has been too readily assumed that carbides are of fairly constant composition. Even if we were to establish the equilibrium composition of alloy carbides in ternary steels as we might do by working out the constitution of the ternary systems (a subject upon which there is little or

no information), we could still not conclude that the carbides in alloy steels showed these compositions. While we might, for instance, assume that the carbide in pearlite formed at a certain subcritical temperature in a manganese steel has a certain manganese content, it would not follow that the carbide formed at another subcritical temperature would have the same composition, nor even that it would have the equilibrium composition, for it does not follow that the equilibrium partition of manganese between ferrite and cementite will be obtained during the formation of pearlite. Information on this point would be very useful in developing sound ideas concerning the factors affecting the rate of growth of pearlite. Such studies, of course, would require the development of suitable analytical methods, as stated above.

It might be pointed out that the greater tendency of manganese than nickel to form carbides is not reflected in the diffusion data presented in these two papers.

The Structure and Properties of Some Iron-nickel Alloys

BY G. SACHS,* MEMBER, AND J. W. SPRETNAK,† STUDENT ASSOCIATE A.I.M.E.

(Cleveland Meeting, October 1940)

THE iron-rich iron-nickel alloys have attracted considerable academic interest in recent years. The carbon-free alloys are of minor practical importance, but they are

10 per cent Ni) undergo the allotropic transformation extremely sluggishly, both on heating and cooling, showing a large hysteresis,² which is not dependent upon

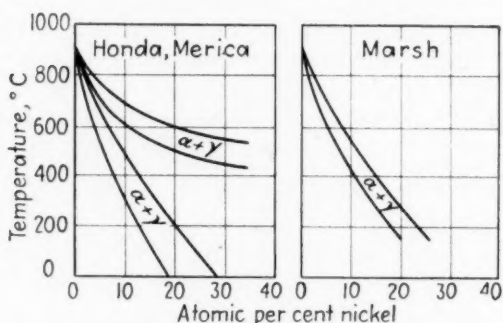


FIG. 1.

FIG. 2.

FIG. 1.—HONDA'S AND MERICA'S IRON-NICKEL DIAGRAM.

FIG. 2.—MARSH'S IRON-NICKEL CONSTITUTIONAL DIAGRAM.

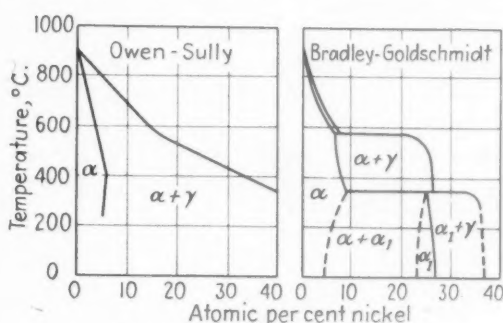


FIG. 3.

FIG. 4.

FIG. 3.—OWEN AND SULLY'S IRON-NICKEL CONSTITUTIONAL DIAGRAM.

FIG. 4.—BRADLEY AND GOLDSCHMIDT'S IRON-NICKEL CONSTITUTIONAL DIAGRAM.

the base of many alloys with various outstanding properties. The iron-nickel alloys, therefore, have been investigated extensively regarding both their structures and their properties. The researches on these alloys up to 1938 have been collected and critically reviewed by J. S. Marsh,¹ and will be discussed in some detail in the sections of this paper dealing with specific subjects.

These numerous investigations have not succeeded in establishing the equilibrium conditions in this system. Alloys containing more than a certain amount of nickel (8 to

the rate of cooling and persists even with very slow rates of cooling.³ Honda² and Merica⁴ have therefore resigned themselves to proposing a diagram (Fig. 1) for practical use, illustrating the structural relations under commercial conditions instead of attempting to establish the true equilibrium diagram. Marsh is less pessimistic and suggests an equilibrium diagram (Fig. 2) which conforms approximately to the facts known about this system. Recent X-ray investigations by Owen-Sully⁵ and Bradley-Goldschmidt⁶ on powdered alloys indicate that the previous work on the iron-nickel system yielded very incomplete results. These investigators agree (Figs. 3 and 4) that alloys in the powdered form containing more than 8 per cent and up to about 35 per cent Ni decompose into a stable heterogeneous mix-

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¹ References are at the end of the paper.

ture of the alpha and gamma phases (ferrite and austenite) if held for a very long time at a temperature of approximately 750°F. (400°C.). Their opinions on the equilibrium conditions at still lower temperatures differ considerably. Owen considers the alpha crystals found in quenched or furnace-cooled alloys a metastable phase containing more nickel than corresponds to the equilibrium composition (6 per cent), while Bradley assumes the formation of an ordered phase, α_1 (Fe_3Ni), containing approximately 25 per cent Ni.

However, the actual results of these two researches do not differ as much as their suggested diagrams indicate. The alloys that have been found to be heterogeneous (alpha + gamma) after prolonged heating fit very well in a diagram of the previously assumed type (Fig. 5). Only their results obtained at the highest temperatures, above 900°F. (500°C.), must be discarded; and this is certainly permissible as the structure may easily change on cooling from such high temperatures. The diagram newly proposed by the authors (Fig. 5) differs from the Owen and Bradley diagrams mainly in that at room temperature the alpha phase is assumed to be the stable phase up to very high nickel contents.

The structure and properties of the carbon-free iron-nickel alloys are according to the present conception determined by the increasing sluggishness of the gamma-alpha transformation with increasing nickel content. This permits a subdivision of the alloys into four groups.

Group 1.—Group 1 contains pure iron and alloys up to approximately 10 per cent Ni. The alloys transform on slow cooling to room temperature completely into ferritic alpha, while martensitic alpha is formed on quenching to an increasing extent with increasing nickel content. Even commercially pure iron appears to exhibit a specific type of martensitic structure on quenching.^{7,8}

Group 2.—Alloys containing between 10

and 25 per cent Ni attain invariably a martensitic structure on cooling down to room temperature. Austenite may be retained on cooling from high temperatures⁶

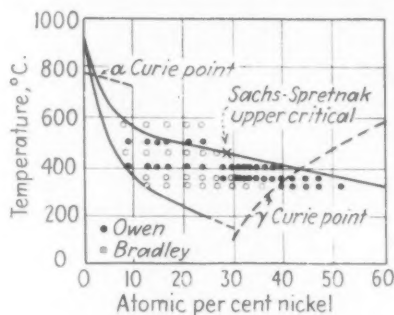


FIG. 5.—IRON-NICKEL CONSTITUTIONAL DIAGRAM SUGGESTED BY AUTHORS, AND COMPARED WITH OWEN'S, BRADLEY'S, AND THEIR OWN EXPERIMENTAL RESULTS.

but appears to have little effect on the structure and the properties. The high hardness and strength of these alloys depend little upon their treatment.

Group 3.—Alloys with about 30 per cent Ni are generally considered to consist of austenite at room temperature, which is unstable. They may be partially transformed from the nonmagnetic gamma into magnetic (martensitic) alpha, both by cooling to very low temperatures (Fig. 1) and by cold-work.⁹ Such alloys occasionally have been found to be slightly magnetic; and, according to Owen's experiments, this may be explained by the peculiar fact that these alloys retain less austenite if heated to high temperature than to comparatively low temperatures, around 1100°F. (600°C.). The alloys of this group are particularly interesting, as they are of the same basic type as the austenitic stainless steels (18 per cent Cr, 8 per cent Ni), which also are unstable in a manner that closely corresponds to the instability of the iron-nickel alloys of this group.

Group 4.—Alloys containing more than 35 per cent Ni have been considered up to the present time as stable austenitic alloys of the pure nickel type. However, Owen⁵ and Bradley⁶ have shown that the proper-

ties of alloys containing less than 50 per cent Ni may be affected by a decomposition into alpha plus gamma and a gradual reformation of gamma on heating. These processes require an extremely long time at temperature even in the powdered alloys, therefore it is questionable whether they are of any practical importance.

tion treatments. The heats were than cast into 4 by 4-in. ingot forms and subsequently reduced by forging to 2 by 2-in. bars, after which sections were cut off and further forged to 3 by 1/2-in. slabs, which constituted the as-received condition.

These forged slabs were first annealed at 1650°F. (900°C.), for 30 min., followed by

TABLE 1.—*Analyzed Composition of the Iron-nickel Alloys Investigated*

Designation	Composition, Per Cent						
	Ni	Fe	Mn	C	P	S	Si
Pure iron.....			0.17	0.04	0.01	0.03	0.04
Alloy:							
4 per cent.....	4.04			0.02			
8 per cent.....	7.98						
16 per cent.....	16.30		0.18	0.04			0.07
22 per cent.....	21.81			0.02			
28 per cent.....	27.88		0.18				
36 per cent.....	35.64			0.03			
42 per cent.....	41.79			0.02			0.08
60 per cent.....		39.18		0.02			
80 per cent.....		20.16	0.20	0.01			
Pure nickel.....		0.18		0.01			0.06

According to this short survey, many questions regarding the structure and properties of iron-rich iron-nickel alloys remain as yet unanswered. The present investigation was undertaken for the purpose of increasing our knowledge of this system by means of various systematic investigations. The effect of cold-work and different heat-treatments on iron-rich iron-nickel alloys, and particularly on an "austenitic steel" containing 28 per cent Ni, has been followed up by means of X-ray and metallographic investigations, hardness tests and coercive-force measurements.

MATERIALS AND EXPERIMENTAL PROCEDURE

For these investigations, 11 iron-nickel alloys were used, ranging in composition (Table 1) from 0 to approximately 100 per cent Ni. The alloys were furnished by the Research Laboratories of the International Nickel Co. at Bayonne, N. J. Basic charges of Armco iron and electrolytic nickel were melted in a 30-lb. high-frequency induction melting unit, followed by suitable deoxida-

furnace-cooling, and conditioned by grinding. For the X-ray investigations, specimens taken from these slabs were then cold-rolled by about 95 per cent reduction, from about 3/8 in. to a thickness of 0.017 in. Photomicrographs, hardness tests and coercive-force measurements were taken on specimens subjected to the following treatment: (1) rolling the slabs to 0.250 in. in thickness; (2) annealing at 1650°F. (900°C.) for 30 min.; (3) specimens then differently cooled from this temperature, rolled to 0.067 in. corresponding to a 75 per cent reduction in thickness, and finally subjected to various heat-treatments.

"Powder diagram" X-ray pictures were taken on specimens rolled to 0.17 in. thick and reduced to a thickness of 0.001 to 0.002 in. by pickling in a mixture of nitric and hydrochloric acids. A General Electric diffraction unit equipped with a molybdenum target tube was used, the flat specimens being mounted in the center of a half-circular vertical cassette with a radius of 80 mm. The conditions of exposure were 160 kv., 24 ma., 2 to 3 hours.

Preferred orientation determinations were made with the same specimens and equipment, using the flat-type cassette with a distance of 40 mm. from specimen to film. A number of specimens were investigated with the X-ray beam perpendicular to the rolled surface (the rolling direction being generally vertical in the photograms). Several specimens were rotated by means of a goniometer head in steps of 5° to 15° about both the rolling and the transverse directions, and from the 10 to 20 photograms obtained in this way the pole figures were constructed. Some results obtained by this procedure have been reported previously.¹³

Coercive-force measurements were performed with a specimen 1.25 by 0.125 by 0.067 in. in dimension. The coercimeter utilized was of the type employed in the Bureau of Mines investigations [*Min. and Met.* (1936) 17, 261]. The coercive-force values are expressed in arbitrary units, in which one unit is equivalent to 22.8 oersteds.

X-RAY INVESTIGATIONS Powder Diagrams

X-ray powder diagrams were taken particularly for the 28 per cent alloy, which is

known to exist as well in the alpha as in the gamma state under conditions of commercial treatment (Figs. 6 and 8). As it is well known that cold-work increases the rate of

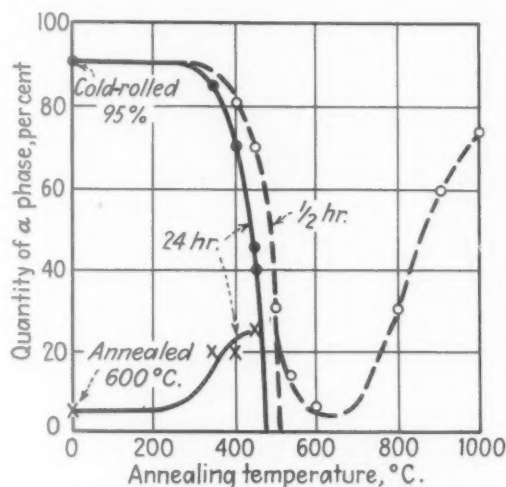


FIG. 6.—QUANTITIES OF ALPHA PHASE IN THE 28 PER CENT IRON-NICKEL ALLOY, OBTAINED AFTER VARIOUS TREATMENTS, ESTIMATED FROM X-RAY DIFFRACTION PATTERNS.

reaction, the majority of the X-ray pictures have been taken on specimens reduced 95 per cent by rolling from the hot-worked and annealed condition and then subjected to various heat-treatments. Such pictures gen-

TABLE 2.—Proportions of Alpha and Gamma in a 72 Per Cent Iron, 28 Per Cent Nickel Alloy Subjected to Various Treatments

Treatment			Alpha, Per Cent	Gamma, Per Cent	Remarks
1. Rolled, Per Cent	2. Hours	3. Hours			
95			90	10	Preferred orientation of alpha
95	350°C., 24		85	15	Strongly ferromagnetic
95	400°C., 1/2		80	20	Strongly ferromagnetic
95	400°C., 24		70	30	Strongly ferromagnetic
95	450°C., 1/2		90	10	Strongly ferromagnetic
95	450°C., 1/2		70	30	Strongly ferromagnetic
95	450°C., 24		45, 40	55, 60	Strongly ferromagnetic
95	500°C., 1/2		30	70	Strongly ferromagnetic
95	550°C., 1/2		15	85	Strongly ferromagnetic
95	600°C., 1/2		5	95	Slightly magnetic
95	800°C., 1/2		30	70	Strongly magnetic, gamma lines spotty
95	900°C., 1/2		60	40	Strongly magnetic, gamma lines spotty
95	600°C., 1/2	350°C., 24	20	80	Weakly magnetic
95	600°C., 1/2	400°C., 24	20	80	Weakly magnetic
95	600°C., 1/2	450°C., 24	25 ?	75	Weakly magnetic
95	900°C., 1/2	350°C., 24	40	60	Gamma lines spotty
95	900°C., 1/2	400°C., 24	55	45	Gamma lines spotty
95	900°C., 1/2	450°C., 24	35	65	Gamma lines spotty

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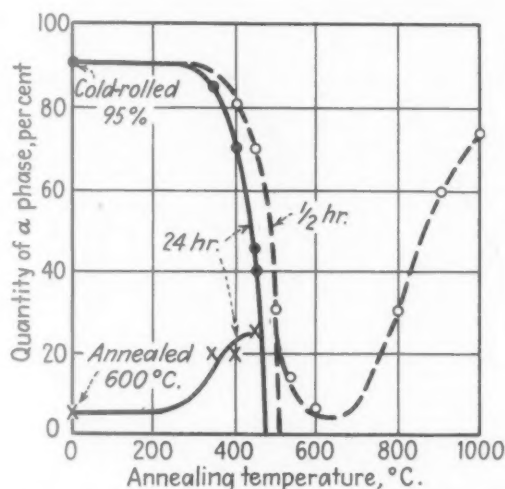


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95	450°C., 1/2		70	30	Strongly ferromagnetic
95	450°C., 24		45, 40	55, 60	Strongly ferromagnetic
95	500°C., 1/2		30	70	Strongly ferromagnetic
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95	600°C., 1/2		5	95	Slightly magnetic
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95	900°C., 1/2		60	40	Strongly magnetic, gamma lines spotty
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95	600°C., 1/2	400°C., 24	20	80	Weakly magnetic
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95	900°C., 1/2	400°C., 24	55	45	Gamma lines spotty
95	900°C., 1/2	450°C., 24	35	65	Gamma lines spotty

erally show alpha and gamma lines in varying proportions, enabling the estimation of the relative proportions of the two phases. This estimate has been performed

Table 2 and Fig. 6 permit the conclusion that severely cold-worked iron-nickel alloys behave in the same manner as the powdered specimens on which the recently suggested

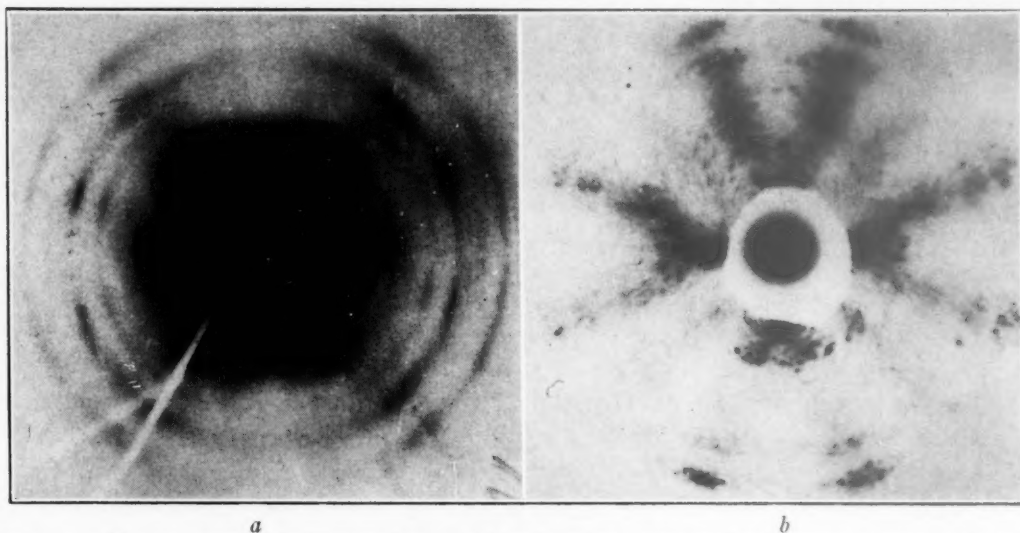


FIG. 7.—X-RAY FIBRE PATTERNS OF A 60 PER CENT IRON-NICKEL SHEET AFTER VARIOUS TREATMENTS.

a, cold-rolled 95 per cent.

b, annealed at 1650°F. (900°C.) for 1/2 hour.

independently by two workers, each estimating three times. The resulting values were averaged. Table 2 and Fig. 6 summarize the results obtained by this method. These values, however, are not very accurate, probably not closer than ± 5 per cent, as the individual lines were often found to be rather irregular. In some cases the diagrams did not appear to be symmetrical, and this condition may indicate a nonuniform state of the respective specimen. The relative intensities of the different alpha lines in the cold-rolled and tempered conditions are also affected by the presence of a pronounced preferred orientation (see next section), while the gamma lines in the specimen annealed at high temperatures are generally spotty, indicating the presence of large recrystallized grains.

The total absence and the presence of small amounts of the alpha phase in the 28 per cent alloy can be also detected definitely by the absence or presence of ferromagnetism.

equilibrium diagrams, Figs. 3, 4 and 5, are based. The pure austenitic condition of the 28 per cent alloy may or may not be obtained on cooling (any type) from comparatively low temperatures, 1300°F. (700°C.), while cooling from a temperature of 1470°F. (800°C.) and higher generally results in a heterogeneous condition containing a substantial portion of the metal in the alpha condition. The extent of this decomposition is also affected by other factors. (See section on hardness.) Extensive cold-rolling produces an almost 100 per cent alpha condition (Fig. 9). Annealing such specimens does not change the structure up to about 660°F. (350°C.). Annealing at 750°F. (400°C.) for 24 hr. causes a slight but definite increase of the proportion of gamma. After tempering at 840°F. (450°C.) for 24 hr., 50 per cent of the metal is again in the gamma condition, while at 930°F. (500°C.) almost pure gamma may be obtained within a time ranging from 1/2 to 24 hours.

It is thus definitely established that the upper critical temperature for this alloy is at a temperature below 930°F. (500°C.), and probably at about 880°F. (470°C.).

The specimens annealed at a temperature of 1010°F. (600°C.) for ½ hr. were about 95 per cent austenitic and slightly magnetic. Subsequent anneals for 24 hr. at

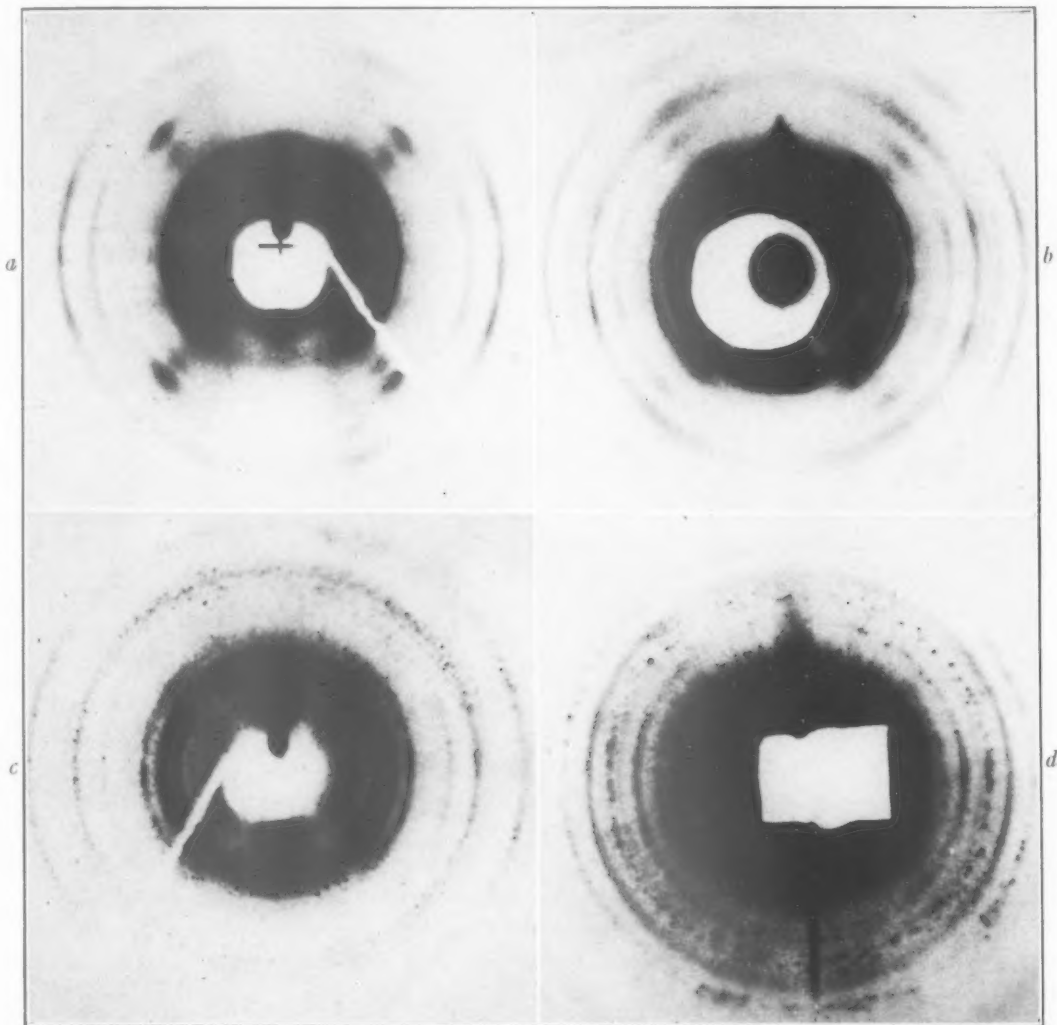


FIG. 8.—X-RAY FIBRE PATTERNS OF A 28 PER CENT IRON-NICKEL SHEET AFTER VARIOUS TREATMENTS.

- a, cold-rolled 95 per cent.
- b, annealed 930°F. (500°C.) for ½ hour.
- c, annealed 1110°F. (600°C.) for ½ hour.
- d, annealed 1650°F. (900°C.) for ½ hour.

This corresponds closely to the results of Owen,⁵ while Bradley⁶ sets this limit at 660°F. (350°C.) in spite of the fact that a specimen annealed for a long time at a temperature of 840°F. (450°C.) was still found to be slightly heterogeneous.

temperatures between 660° and 840°F. (350° and 450°C.) developed in every case a considerably larger amount of alpha, estimated to 10 to 15 per cent. To check this result more conclusively, a specimen that had been reduced 75 per cent by rolling and

water-quenched from 1390°F. (700°C.) was annealed subsequently at a temperature of 750°F. (400°C.) for 24 hr. The specimen was totally austenitic and nonmagnetic

cent alloy should retain permanently any structure developed by a previous treatment on subsequent heating to temperatures between 120° and 840°F. (50° and

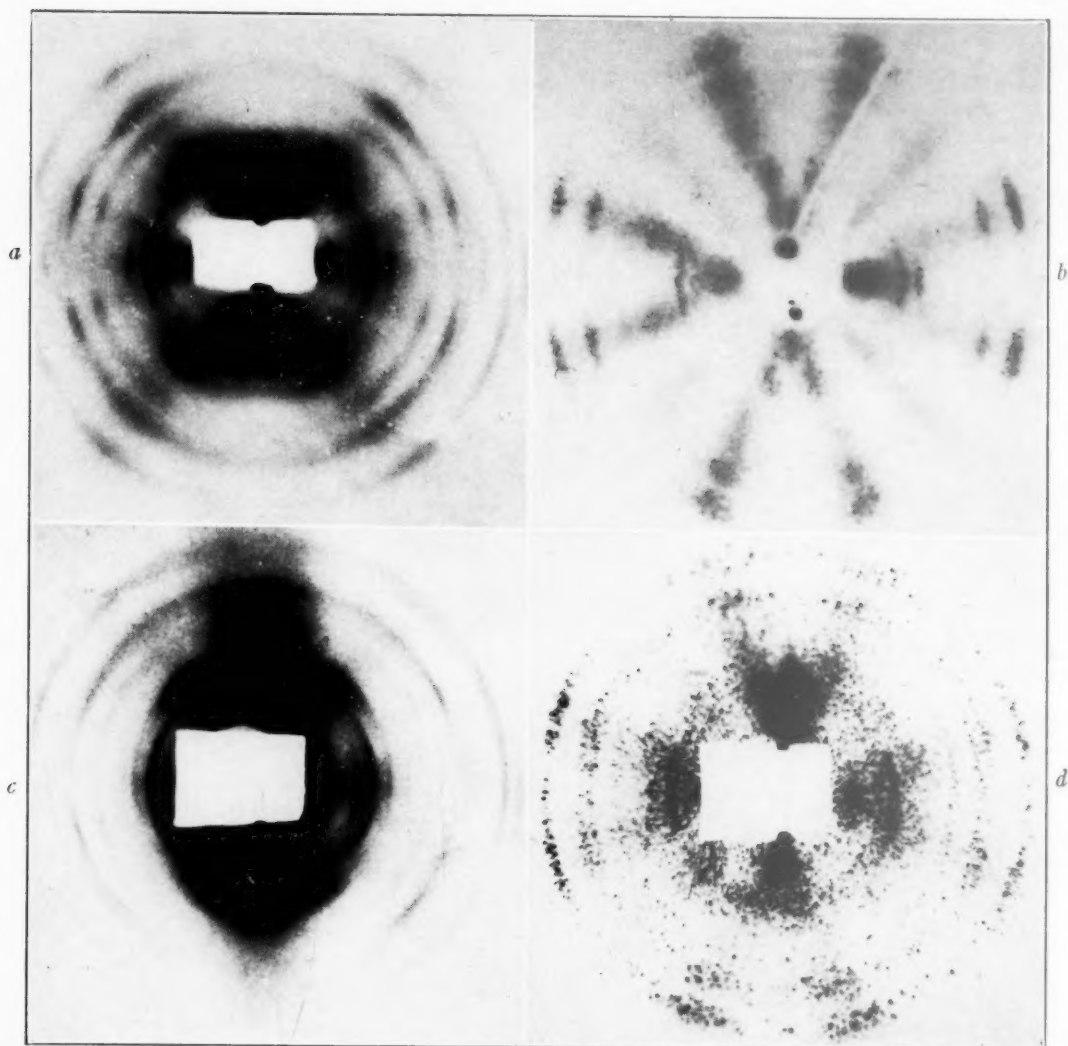


FIG. 9.—X-RAY FIBER PATTERNS OF 36 PER CENT IRON-NICKEL SHEET AFTER VARIOUS TREATMENTS.

- a, cold-rolled 95 per cent.
- b, annealed at 1650°F. (900°C.) for ½ hour.
- c, annealed at 750°F. (400°C.) for 24 hours.
- d, annealed at 1650°F. (900°C.) for ½ hour.

after quenching from 1390°F. (700°C.) but developed a considerable magnetism after the subsequent anneal at 750°F. (400°C.). This result is not consistent with the old conception of the transformation in iron-nickel alloys. According to Fig. 1 the 28 per

450°C.). It has been also previously denied³ that the transformation is influenced by the rate or time of heating. The presented experiments, however, prove definitely that both the transformations of the alpha and gamma states toward heterogeneous equi-

librium conditions may start in a 28 per cent alloy at a temperature as low as 660°F. (350°C.). This is particularly true for cold-worked metal, while with an annealed metal and regular rates of cooling the alpha-gamma transformation will be detectable only at considerably higher temperatures.

The heterogeneous specimens obtained on heating to 1650°C. (900°C.) did not yield clear results on low-temperature treatments. The spotty condition of the gamma lines in the photographs renders the comparatively small changes uncertain.

No definite conclusion regarding the lower critical temperature can be drawn from these experiments; or, in fact, from any investigation made up to the present time. However, it has been observed that on rolling the structure transforms continuously toward a 100 per cent martensitic alpha condition. It may be concluded therefore that the alpha state is the stable condition at room temperature and the slightly elevated temperatures that are produced during the rolling procedure.

No traces of alpha crystals could be detected in the X-ray photograms of the 36 per cent alloy, in the as-rolled (95 per cent reduction) and at different temperatures for 1/2-hr. annealed condition. A cold-rolled specimen, however, that was subjected to an anneal at 750°F. (400°C.) for 24 hr. showed traces of the alpha phase present (Fig. 9). Thus, the 36 per cent alloy is also unstable within a certain temperature range, and the upper critical temperature is somewhat higher than 750°F. (400°C.). This statement agrees well with the results obtained by Owen and Sully.⁵

X-RAY INVESTIGATIONS ON PREFERRED ORIENTATION

Some additional information on the structures of the 28, 36 or 60 per cent alloys has been obtained from the investigation of the cold-rolled (95 per cent) specimens and the subsequently annealed specimens (Figs.

7 to 9) regarding the preferred orientation of the crystals ("fiber structure").

The austenitic 60 per cent alloy shows (Fig. 7) the rolling structure that is characteristic for a number of face-centered cubic metals. This structure remains unchanged up to an annealing temperature of 960°F. (500°C.). On annealing at higher temperatures, a very pronounced "cubic" recrystallization structure is developed,^{10,11,12} which becomes more and more perfect with increasing temperature in spite of the gradual coarsening of the alloy.

The 36 per cent alloy (Fig. 9) behaves usually the same way as the 60 per cent alloy, and, perhaps even more perfectly, exhibits both the rolling and the recrystallization textures (these structures have been analyzed in detail and previously described¹³). The identical structures of the two austenitic alloys investigated can be taken as a definite proof that the gamma state of the 36 per cent alloy is almost completely retained during rolling and annealing under conditions corresponding to those used in commercial practice. Generally, even very small amounts of a second phase disturb the formation of a pronounced recrystallization structure on annealing.¹¹ Therefore it is very improbable that the special expansion properties of this alloy can be explained by the gamma-alpha reaction, as suggested by Bradley. Generally in iron-nickel alloys the latter reaction is not reversible and depends considerably upon the extent of strain-hardening, therefore it cannot account for the characteristic reversible expansion of these alloys, which depends little upon their previous history. The expansion is also particularly abnormal at temperatures close to room temperatures, while any gamma-alpha transformation is extremely slow below 660°F. (350°C.) (Fig. 6).

A few additional experiments with the 36 per cent alloy were performed to determine the effect of the transformation products on the development of the recrystalliza-

tion structure. Annealing the rolled condition at a temperature of 750°F. (400°C.) for 24 hr. develops, as discussed in the previous section, a small amount of alpha crystals. The rolling structure is considerably changed by this process (Fig. 9c). It appears that most of the gamma crystals in the cubic orientation have been transformed into alpha, while the remaining orientations are little affected. Annealing this condition at 1650°F. (900°C.), for ½ hr. yields the cubic structure much less pronounced (Fig. 9d) than the regular annealing treatments (Fig. 9b). Thus, the development or presence of a small amount of alpha crystals considerably disturbs the formation of a pronounced recrystallization structure.

The 28 per cent alloy behaves very differently as compared with the two austenitic alloys. The rolling structure corresponds, according to the X-ray photogram (Fig. 8), closely to that of regular alpha iron and steels.^{14,15,16} The martensitic alpha crystals in the alloy, therefore, have the same crystallographic characteristics as any ferritic alpha crystals; and a sufficient quantity must have been formed early enough on cooling and on rolling to be lined up perfectly during the subsequent rolling. Generally at least 75 per cent reduction is required to produce a rolling structure as perfect as that obtained in the present investigation.¹⁰ On annealing (½ hr.) the gamma phase becomes first apparent at a temperature of 840°F. (450°C.) but has little influence on the rolling structure, while at a temperature of 930°F. (500°C.) the gamma phase is predominant and the X-ray photogram becomes rather complicated. This picture still shows the pattern belonging to the alpha crystals in the preferred rolling orientation, while another strong and regular pattern is superimposed owing to a preferred orientation of the gamma crystals. The crystallographic nature of the latter pattern has not yet been determined. There is the probability that

the orientation of the gamma crystals is correlated with that of the alpha crystals according to the shear mechanism that has been found to be the general manner of the martensitic transformation from gamma to alpha and alpha to gamma in carbon steels^{17,18} and iron-nickel alloys.¹⁹ However, it appears also possible that the gamma crystals prefer an orientation corresponding to the previously discussed rolling structure of the austenitic alloys. This question can only be decided by a special investigation. After annealing at a temperature of 1110°F. (600°C.) the 95 per cent rolled specimens are recrystallized and, as previously mentioned, completely transformed into the gamma state. The crystals still show a residual preferred orientation corresponding to that of the gamma crystals in the specimen annealed at 930°F. (500°C.). Annealing at still higher temperatures, such as 1650°C. (900°C.) again results in a mixture of recrystallized rather large gamma crystals, and distorted alpha crystals, the latter yielding continuous lines in the X-ray photograms. There is little preferred orientation detectable in such pictures (Fig. 8d).

MICROSTRUCTURE

The microstructures of the alloys are fully explained by our present knowledge about the iron-nickel system. The slowly cooled alloys with nickel contents up to 8 per cent show a ferritic structure. The grain size gradually decreases with increasing nickel content, and there is also a noticeable tendency to develop ragged grain boundaries and subdivided (martensitic?) grains. The structure of the pure iron in the quenched condition is very similar to those of the 4 and 8 per cent alloys obtained on slow cooling, while the 8 per cent alloy develops a peculiar structure on quenching which is both similar to the martensite in carbon steel and to the duplex structure in other heat-treatable alloys, such as alpha-beta brass. Sets of irregular parallel and intersecting plates are obviously formed

within each austenitic grain and often limited by the straight boundaries of original twins. The 16 and 22 per cent alloys invariably exhibit the structure that is

The austenitic alloys of group 4, containing 36 to 100 per cent Ni, represent in both the annealed and cold-rolled conditions the general trend of solid solution alloys. The

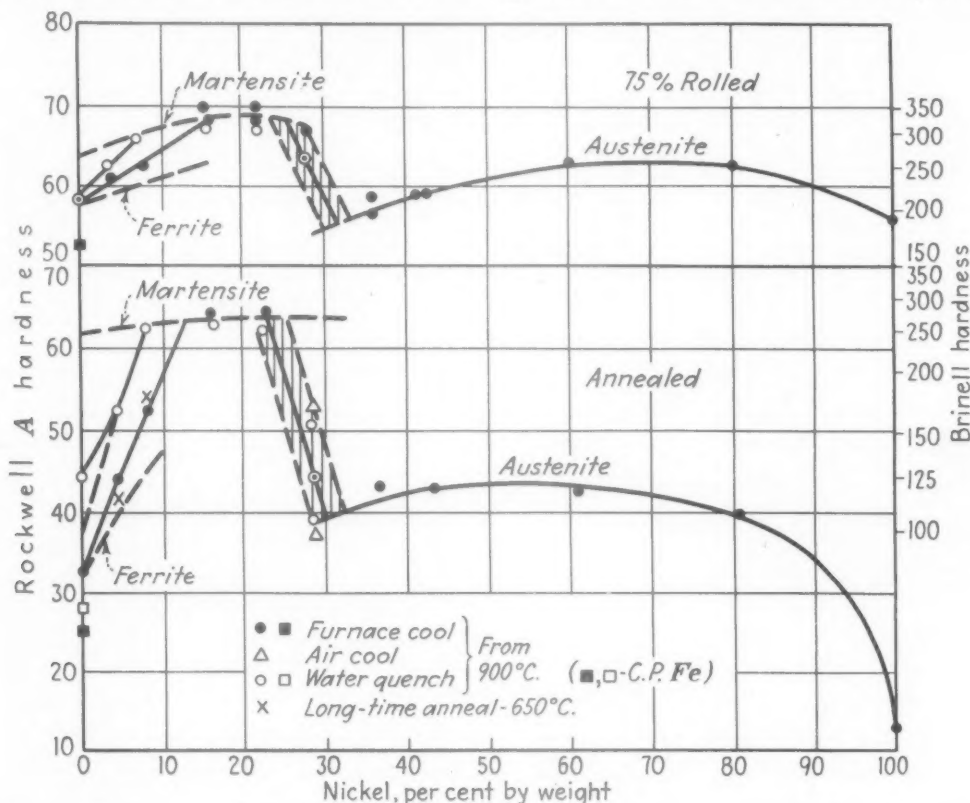


FIG. 10.—EFFECTS OF COLD-ROLLING, ANNEALING, AND QUENCHING ON HARDNESS OF IRON-NICKEL ALLOYS.

generally designated as martensitic. The original austenitic grains appear transformed to an interwoven mass of alpha crystal plates. Whether austenite is retained to a certain extent cannot be definitely stated from this structure.

HARDNESS

The hardness values that can be obtained with iron-nickel alloys under varying conditions are summarized in Fig. 10. Fig. 11 shows the effect of annealing and different types of cooling on the hardness of specimens that have been reduced 75 per cent in thickness by rolling from the annealed condition, furnace-cooled from 1650°F. (900°C.).

hardness is lowest for the pure nickel and reaches a flat maximum at compositions of 50 and 70 per cent Ni for the annealed and the cold-rolled conditions, respectively. The annealing curves for these alloys are also characteristic for simple metals. The softening of pure nickel suddenly begins at a temperature of about 1020°F. (500°C.), while the alloys soften more gradually at temperatures above the same limit. The initial hardening of all the austenitic alloys on annealing at temperatures around 930°F. (500°C.) has not been explained as yet. This effect is particularly pronounced in the 60 and 80 per cent alloys and may be related to the ordering process (superstructure) that has been observed in these alloys.¹

The general hardness relations in the iron-rich alloys can be best explained by the assumption that the properties of the annealed and heat-treated alloys are limited

peratures). In the higher nickel irons also, the presence of gamma may affect the properties.

As already discussed in relation to the

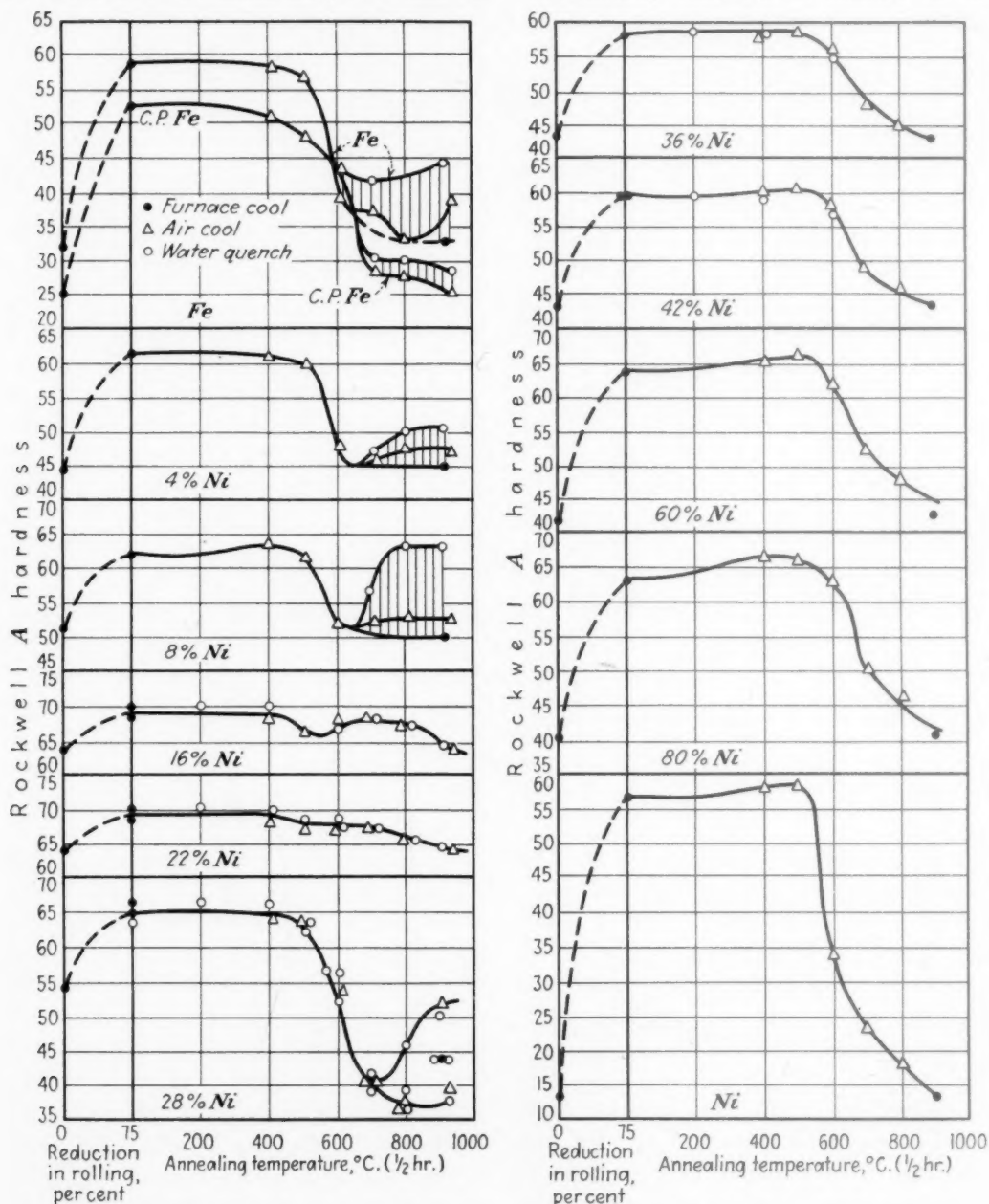


FIG. 11.—DECREASE IN HARDNESS ON ANNEALING COLD-WORKED IRON-NICKEL ALLOYS.

by the two rather definite structural states of the alpha phase, the soft ferritic equilibrium condition and the hard martensitic condition (diffusionless formed at low tem-

microstructure, pure iron has little capacity to form martensite, while the alloys approach gradually the martensitic condition with increasing nickel content. The alloys

of group 1 are still in a more or less ferritic condition on slow cooling. The 8 per cent alloy, however, becomes on quenching almost as hard (250 to 275 Brinell units) as the alloys of group 2, which are martensitic in both the quenched and slowly cooled conditions. The presence of the gamma phase in these alloys apparently only little affects the hardness, but the comparatively low hardness of the quenched 22 per cent alloy is certainly related to the increasing tendency to retain gamma with increasing nickel content.

Cold-work (75 per cent reduction in rolling) has greater hardening effect on the alloys of groups 1 and 2 the more ferritic is the initial condition. The hardness of the cold-worked martensitic alloys reaches values between 275 and 350 Brinell units while the cold-worked ferritic alloys become as hard as 200 to 250 Brinell units. Surprisingly, the martensitic alloys can be rolled almost as easily as the ferritic alloys, and this behavior may be related also to their low strain-hardening capacity. Thus, the hardening effects of both cold-work and heat-treating are not additive, but the cold-work rather affects the hardness of the martensitic alloys in a manner similar to that of already highly strain-hardened alloys.

The annealing curves for the alloys of group 1 show the gradual reduction of the lower critical temperature (on heating) with increasing nickel content. While rolled pure iron may recover from strain-hardening by a "process anneal" below the critical range, the beginning transformation interferes with the softening of the 4 and 8 per cent alloys. However, the hardness obtainable by process annealing is practically the same as that resulting from a furnace cool from temperatures above the critical range.

A long-time anneal was carried out with the 4 and 8 per cent alloys at 1200°F. (650°C.) for 24 hr. This procedure but very little softened the 4 per cent alloy, while the

8 per cent alloy had been slightly hardened. The latter effect can be explained by the starting alpha-gamma transformation. It is not possible, therefore, to eliminate completely the effect of the transformation or of previous cold-work on the hardness of some of the iron-nickel alloys. Therefore, the question to what extent the effect of nickel on the hardness of iron is caused by solid solution and by transformation hardening, respectively, cannot be definitely decided. Probably, however, the latter process contributes considerably to the total hardness. Cold-worked iron is softened by increasing the annealing temperature from 1110° to 1470°F. (600° to 800°C.) by about 30 Brinell units, while the 8 per cent alloy has already attained its minimum hardness at 1110°F. (600°C.). This difference of 30 hardness units determines the hypothetical hardness of soft ferritic iron-nickel alloys²⁰ approximately as indicated in Fig. 10.

The difference between the hardness curves for pure iron in the slowly cooled and the water-quenched conditions, respectively, can be only partly attributed to the effect of the gamma-alpha transformation. This difference is observed also if cooled from a temperature below the critical and generally is considered to be a solid solution and precipitation effect, due to the presence of a small amount of carbon.²¹ The quenched pure iron exhibits a further increase in hardness on aging at room temperature, owing to the well-known "quench aging." In addition to pure iron, the two alloys containing 4 and 8 per cent Ni, respectively, have been investigated for their quench-aging capacity. However, only the (commercially) pure iron has been found to exhibit quench-aging, while the hardness of both nickel-containing alloys is not affected by quenching from a temperature below the lower critical and subsequent aging. Such a behavior was not expected as, according to a recent investigation by Andrews and Trent,²² only carbide-forming

alloying elements such as molybdenum reduce the quench-aging tendency of iron, while ferrite formers such as silicon and aluminum have been found to be practically without influence. Nickel is generally considered to belong to the group of the ferrite formers that have no power to form carbides in presence of iron.²⁰

Another interesting fact is that aging after quenching from 700°C. is more pronounced than after quenching from 900°C. As pure iron also shows a partly martensitic structure on quenching this "martensite" obviously is less susceptible to precipitation-hardening than the ferrite crystals formed on slow cooling or on recrystallization, respectively. Thus, the effect of the carbon solution and of the "martensitic" structure on the hardness of alpha iron may be separated, as quenching from 900°C. increases the hardness by only about 10 Brinell units above the hardness on quenching from 700°C., while the total effect of quenching is more than 40 Brinell units. This last effect, therefore, must be attributed principally to aging and not to the martensitic structure (Fig. 10).

For the sake of completeness, the strain-aging after rolling the pure iron and the 4 per cent alloy by 10 per cent reduction and heating to 100°C. for up to 24 hr. has been also determined. For both alloys, a comparatively small maximum aging effect of about 15 Brinell units was found. There is, therefore, apparently no parallelism between quench-aging and strain-aging, which must be of different origins.

To determine in a more accurate manner the effect of quenching on pure iron a few experiments were carried out with a chemically pure sample supplied by Dr. W. P. Sykes, of the Cleveland Wire Division of the General Electric Co. The hardness values obtained on differently treated specimens of the C.P. iron are incorporated in Figs. 10 and 11. This iron is generally considerably softer than the commercial iron, which contains a certain amount of carbon

and other elements. Quenching from temperatures between 1470° and 1700°F. (800° and 925°C.) increases the hardness very slightly but definitely in comparison with the hardness of slowly cooled metal. The magnitude of this effect corresponds fairly well with that derived for the commercially pure iron (Fig. 10).

The particularly interesting hardness results obtained with the 28 per cent alloy, representing group 4, have not been discussed in detail as yet. This alloy may be found on any type of cooling from a temperature of 1110°F. (600°C.) or above either in the gamma condition or as a mixture of gamma and alpha crystals. The factors that control the proportions of the two phases have not been completely established, except for the relation that on cooling from 1110° to 1290°F. (600° to 700°C.) generally a pure gamma condition results, while above this range alpha may be formed on cooling, the quantity increasing with the annealing temperature (Fig. 6). However, the hardness of specimens annealed at temperatures between 1470° and 1700°F. (800° and 925°C.) varies within wide limits, not dependent upon the type of cooling. The hardness values obviously are related to the quantity of alpha present; and with more than 50 per cent alpha (determined by the X-ray investigation) still a rather soft metal with a hardness of about 150 Brinell units is obtained.

The hardening of the 28 per cent alloy by cold-work exceeds that of any other iron-nickel alloy. It has been observed also that the quantity of alpha is considerably increased by the rolling (see section on X-ray investigation). Thus the hardening during rolling results from the combined effect of both strain-hardening and transformation-hardening, and this holds generally true for any of the unstable austenitic steels such as the austenitic stainless steels²³ and the austenitic manganese steels. This explains also the fact that the strain-hardening capacity of such steels decreases with in-

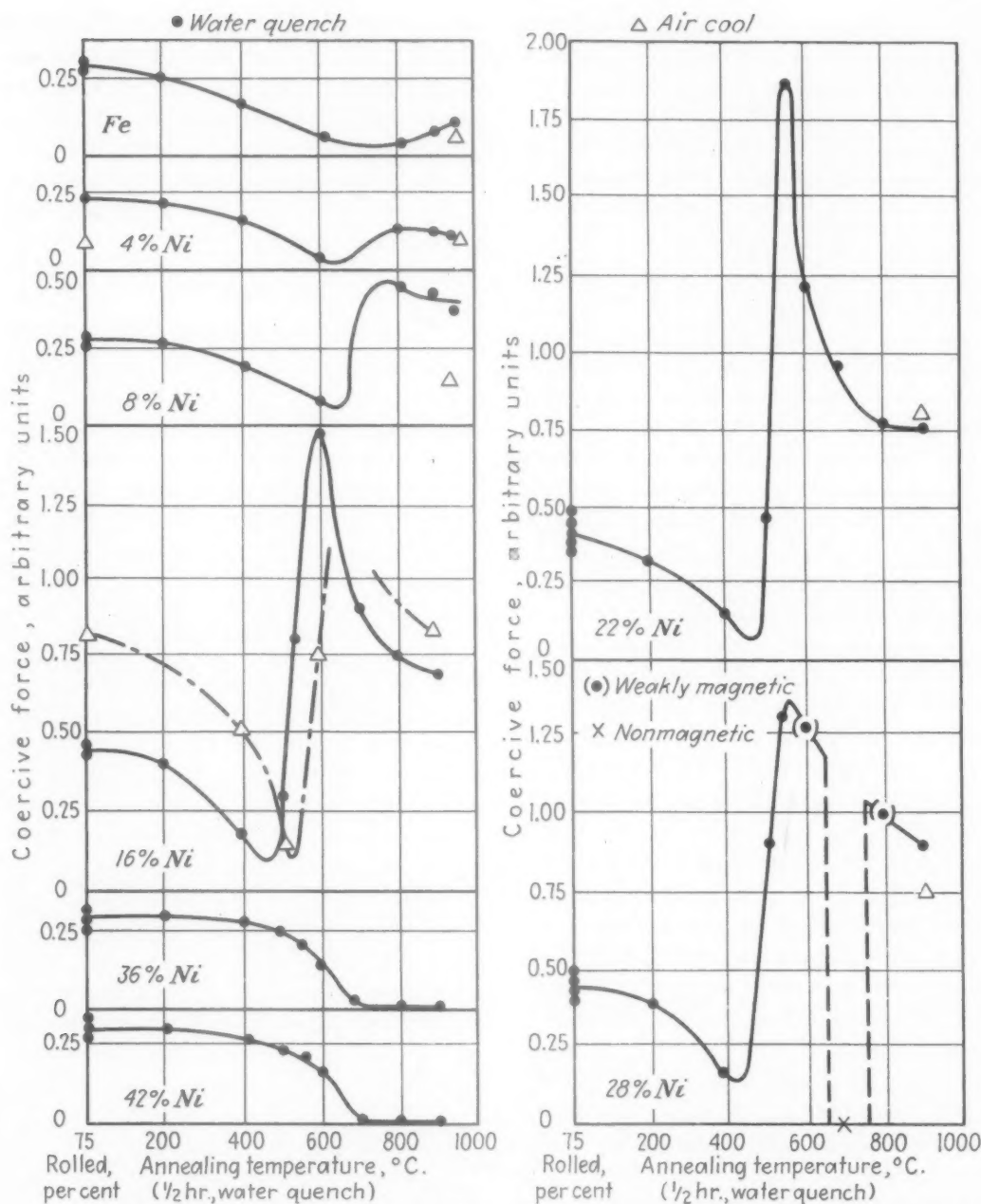


FIG. 12.—CHANGES IN COERCIVE FORCE ON ANNEALING COLD-ROLLED IRON-NICKEL ALLOYS.

creasing stability of the gamma iron, such as produced by an increasing nickel content.^{24,25}

MEASUREMENT OF COERCIVE FORCE

The coercive force of a number of alloys in different conditions is represented in Fig. 12. Specimens rolled by 75 per cent

reduction were annealed for $\frac{1}{2}$ hr. at different temperatures and quenched from the annealing temperature. The changes of the coercive force correspond to the previously discussed changes in structure, but in a manner that cannot be adequately explained as yet. Therefore a detailed discussion of the results presented in Fig. 12 will

be postponed till further experimental material can be made available.

SUMMARY

1. Structural changes toward equilibrium conditions have been observed by means of X-ray investigations in an iron-nickel alloy with 28 per cent Ni, in both the cold-rolled and the annealed conditions. These reactions definitely establish the heterogeneous ($\alpha + \gamma$) equilibrium condition for this alloy for a certain temperature range below an upper critical temperature of 900°F. (480°C.).

2. The 28 per cent alloy tends to transform completely on rolling into the alpha state. It is concluded therefore that the equilibrium condition for this alloy at room temperature and temperatures up to about 400°F. (200°C.) consists of pure alpha.

3. A new equilibrium diagram for the iron-nickel system has been suggested, which explains the data obtained in the present investigation on commercial alloys and previously by Owen-Sully and by Bradley-Goldschmidt on powdered alloys.

4. The hardness values of alloys containing more than 4 per cent Ni are increasingly affected by residual strain-hardening and transformation-hardening, respectively, with increasing nickel content. Hypothetical curves for the hardness of the soft ferrite and the hard martensite have been developed. Alloys containing about 15 to 25 per cent Ni are generally in an almost complete "martensitic" condition. Cold-work hardens ferritic and also austenitic alloys more than the alloys in the martensitic condition. The martensitic alloys also can be cold-worked extensively.

5. The alloy with 28 per cent Ni is strain-hardened to a particularly large extent by cold-rolling, owing to the simultaneous formation of the carbon-free martensite. On heating at a temperature of 1290°F. (700°C.) the very soft and nonmagnetic gamma condition can be obtained, while heating at higher temperatures generally results in a harder mixture of gamma and

alpha crystals. The alpha crystals formed on cold-rolling develop a preferred orientation structure similar to that of ingot iron and steels. Gamma crystals formed at a temperature below the recrystallization limit are also arranged in an orderly manner in a structure, but that has not been investigated as yet.

ACKNOWLEDGMENTS

The authors are indebted to Dr. Paul D. Merica and Dr. A. J. Miller, of the International Nickel Co., for furnishing the alloys used in the investigations with their chemical analyses, and also to Mr. W. W. Culbertson, of the Department of Metallurgy at the Case School of Applied Sciences, for the measurements of coercive force.

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DISCUSSION

(W. P. Sykes presiding)

P. D. MERICA,* New York, N. Y.—All of those interested in iron-nickel alloys will be interested, as am I, in the information and views of the authors with respect to the structure and properties of these important and rather peculiar alloys. In discussing the constitution of the heterogeneous alloys, the authors suggested that Doctor Honda and I had "resigned ourselves" to the use of a double diagram, and I think the use of the word "resigned" was very apt. When faced with the request for a constitution diagram of the iron-nickel alloys for the A.S.M. Handbook, I felt that, in view of the conflicting information available at the time, it was better to give a diagram which (with respect to the heterogeneous alloys) described how they performed under heating and cooling rather than what their equilibrium conditions actually were. The authors' paper has contributed much to the clarification of this system.

The principal peculiarity of the behavior of the low-nickel heterogeneous alloys is, of course, their sluggishness in transforming both on heating and on cooling, and I have always attributed this sluggishness to the low rate of diffusion in these alloys at the temperatures of transformation, and I wonder whether the authors agree with this view. It is interesting in this connection to note that the initiation of transformation (in the alloys containing up to about 28 per cent Ni) either upon heating, or upon cooling, appears to occur at about the temperatures that are shown in the authors' proposed diagram as representing, respectively, the upper temperature limit and the lower temperature limit of the heterogeneous alloys. If, for example, a 20 per cent nickel-iron alloy in the alpha condition is heated, it should begin to transform, according to the authors' diagram, at about 250°C.; such transformation would, however, require diffusion if the transformation substantially reflected equilibrium conditions. In fact, the transformation does not begin normally until a temperature of about 500° is reached, which, according to the authors' diagram, is about the maximum temperature at which both alpha and gamma

alloys can exist in equilibrium. At this temperature transformation from the alpha to the gamma condition can occur without diffusion. It thus appears that under normal rates of heating and cooling, transformation does not occur in the 20 per cent alloy upon heating until it can occur without diffusion, and when this is possible it does occur, although even then it is somewhat sluggish. The lag in transformation in this alloy at temperatures higher than 500° must presumably have another explanation than that based upon sluggishness of diffusion, although even at the latter temperatures there may be minor diffusion processes occurring in consequence of the presence of impurities, including particularly carbon.

I. R. KRAMER,* Washington, D. C.—The authors have used an interesting method in their study of the iron-nickel system. However, their conclusion regarding the stability of the alpha state of the 28 per cent Ni alloy at 180°C. should be further justified as the rolling operation may not produce a state of true equilibrium under ordinary conditions, but a metastable equilibrium under the conditions of pressure and temperature.

Since holding at 350°C. for 24 hr. is hardly sufficient to attain equilibrium, it would be interesting to determine the shift in the percentage of the alpha phase by holding for longer times, as has been found necessary by other investigators.

C. S. SMITH,† Waterbury, Conn.—The authors comment upon the curious behavior shown in Fig. 6, whereby greater amounts of alpha result from quenching the gamma alloys from higher temperatures. I do not think this is entirely or even principally an effect of quenching strains. I suspect that such behavior is a fairly general one and that the rate of decomposition of a solid solution is higher the higher the temperature from which it has previously been quenched. The rate of precipitation of iron from alpha brass is a case in point. In a 70-30 brass containing 0.05 per cent iron quenched from 800°C., precipitation is 90 per cent complete in about 128 hr. at 450°C. If the same alloy is cooled from 800° to 600°C. and then quenched, precipitation has only just

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† Research Metallurgist, American Brass Co.

started in 128 hr. and is only 40 per cent complete in 910 hr. at 450°C. Furnace cooling to 400°C. (below the solid-solubility line) almost completely inhibits subsequent precipitation at 450°C. It seems evident that the distribution of the iron atoms in the solid solution at elevated temperatures is such that subsequent nucleation and precipitation is relatively easy and at lower temperatures the distribution changes in a manner to render subsequent changes much slower. These effects will become less noticeable as the concentration of the solution increases but to some extent should be present generally.

S. R. HOOD,* Detroit, Mich.—We have found that the expansion rate of Invar at room temperature varies when the material is heat-treated between 600° and 1200°F. The expansion coefficient increases progressively from 1×10^{-6} for cold-rolled material to 1.1×10^{-6} when heat-treated for 3 hr. at 700°F. Using higher heat-treating temperatures, the expansion increases abruptly to a maximum of 2×10^{-6} at 875°F. and then decreases gradually on using still higher temperatures until at 1200°F. a value of 1.2×10^{-6} is obtained. This, in general, follows the amount of "cubic recrystallization" shown by your tests at 400° and 900°C.

Is there any relation between the foregoing expansion coefficient changes and the amount of cubic recrystallization described by the authors?

G. SACHS (author's reply).—Dr. Merica suggests, as I understand, that, under regular commercial conditions and with annealed metal, the transformation of the sluggish concentrations between 10 and 30 per cent Ni will not start as long as concentration differ-

ences between the unstable and the stable phase exist. Therefore, the two inner lines of the "commercial diagram" correspond approximately to the equilibrium diagram. Regarding the outer lines or commercial temperatures of the end of transformations, it may be assumed that the transformation of alpha crystals into gamma crystals of identical composition still involves a diffusion process that may require some temperature change or considerable time before it is finished.

I agree with Mr. Kramer's objection that the rolling operation may not produce a state of true equilibrium. However, it is difficult to explain why rolling should transform a stable condition into another one that is unstable at the temperatures developed during rolling. Annealing at a temperature of 350°C. for a long time is also not sufficient to produce equilibrium. Some other investigators have gone as far as holding for half a year at 350°C. without attaining true equilibrium.

I was very much interested to learn from Dr. Cyril Smith that in precipitation-hardenable alloys a high quenching temperature initiates a faster phase change than a low quenching temperature.

Mr. Hood's interesting observations regarding the variation in the expansion rate of Invar do not appear to me related to the precipitation of alpha on annealing. This precipitation is a very sluggish process and should be insignificant under commercial conditions. On the other hand, recrystallization and the associated change in directionality may affect the properties, but the expansion rate of a cubic alloy sheet should be independent of the fiber structure. It would need, therefore, more experimental evidence than is as yet available to determine a relation between expansion properties and fiber structure.

* Chief Engineer, W. M. Chace Co.

Simple Method for Detecting Susceptibility of 18-8 Steels to Intergranular Corrosion

BY H. W. RUSSELL,* MEMBER A.I.M.E., H. PRAY* AND PAUL D. MILLER*

(New York Meeting, February 1941)

It is known that austenitic chromium-nickel steels that have free carbide in the grain boundaries are subject to intergranular corrosion. It is difficult to detect such a susceptible condition in a fabricated article because present test methods require a sample section for examination and in most cases this is difficult to obtain.

The question of the nature and prevention of intergranular corrosion in austenitic stainless steels has been ably discussed by Bain and co-workers¹⁻³ and by other investigators.⁴⁻¹⁰ The present methods of study subject samples to corrosive conditions in such reagents as the Strauss solution, a mixture of copper sulphate and sulphuric acid. Such tests usually require at least 72 hr. to run. Various methods of measuring the degree of sensitization have been employed, such as the measurement of electrical resistivity, magnetic measurements, measurement of the degree of cracking produced on bending over a mandrel, and microscopic studies. The detection of carbides at the grain boundaries by metallographic polishing and etching methods is tedious and requires a skilled operator. A recent report on such methods of carbide detection is given by the American Society for Testing Materials Subcommittee VI of Committee A-10¹¹ and by Arness.¹²

The present investigation was undertaken to develop a simple test procedure for

detecting carbide precipitation or susceptibility to intergranular corrosion. The test is designed for use in the plant and for the testing of fabricated structures.

Carbide precipitation, the factor leading to susceptibility to corrosion, is produced by heating the alloy in the temperature range 800° to 1600°F., as in welding, in improper annealing or in service where such temperatures are met. The connection between such precipitation and susceptibility to corrosion has been thoroughly discussed, as has been the use of stabilizing addition elements to prevent precipitation.

EXPERIMENTAL METHOD

A small area of the steel under test is subjected to an anodic treatment in a cell that can be clamped onto a sample or an actual structure.

The cell and electrical circuit used are illustrated in Fig. 1. The cell *C* is lead, joined to the steel plate *D* and insulated from it by a short piece of rubber tubing *E*. The cell is forced tightly against the steel plate by a spring or clamping device. The seal formed by the rubber against the steel plate is sufficient to retain the liquid bath inside the cell. The spot treated can be made any shape desired, depending on the shape of the rubber gasket. The cell illustrated polishes a circular spot about $\frac{3}{8}$ -in. diameter.

The bath consists of 60 per cent (by weight) sulphuric acid to which is added 5 ml. per liter of Glycyrrhiza extract (U.S.P.). The cell requires about 2 to 2.5

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* Battelle Memorial Institute, Columbus, Ohio.

¹ References are at the end of the paper.

ml. of the bath, which is discarded after each test.

Power may be supplied by a storage battery or a battery-charging rectifier. Fig. 1 illustrates a battery, the current

voltage gradually falls to about 5.0. This is due to the lowering of the resistance in the cell as the bath heats. This resistance drop is equalized by increasing resistance R , so that a constant current flows.

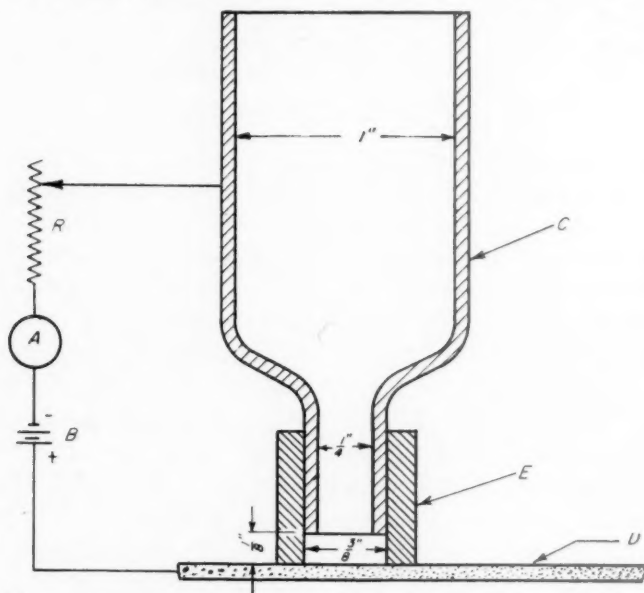


FIG. 1.—DIAGRAM OF CELL AND ELECTRICAL CIRCUIT.

being controlled by the resistance R . The recommended current density is about 14 amp. per sq. in., which for the cell described requires 1.5 amp. at about 5.0 to 6.5 volts. The time used is 3 minutes.

These conditions were chosen after a series of tests was run at current densities of 17.3 amp., 13.9 amp. and 10.4 amp. per sq. in. At 17.3 amp. per sq. in. 2 min. was required to obtain a good polish on unsensitized 18-8. That is, the spots produced by polishing for times less than 2 min. were somewhat frosty in appearance and could be mistaken for an indication of sensitized material. At 13.9 amp. per sq. in. 3 min. was required to obtain a good polish, although a fair polish could be attained in 2 min. At 10.4 amp. per sq. in. at least 5 min. was necessary for a good polish. The current density of 14 amp. per sq. in. and 3 min. were chosen as most practical.

When the cell is operated at 1.5 amp. the initial voltage is usually about 7.4, and the

There is large gas evolution and much bubbling during operation, so the cell was designed to minimize the effect of this bubbling.

The temperature effect is not serious unless the test is being applied to large objects, when the mass of metal is so great that the heat generated in the cell is dissipated rapidly and a poor polish results. This condition can be taken care of in several different ways. One simple method is to heat the object to be tested by running hot water over it until it reaches 120° to 140°F. In this manner the heat drain on the cell is lessened and a correct polish will result. Another is to construct the cell with more than $\frac{1}{8}$ in. between the lead and the sample, and thus generate more heat in the bath due to increased resistance. A third is to increase the current density when testing large objects. The third method must be used with care because there is the possibility of polishing sensitized material if too

much time or current is used. A little experimentation will indicate the best condition to use for an object of a particular size. All tests to be described later were made under the same conditions.

heat-treatments. Whenever possible the samples were water quench-annealed after heating at 2100°F . for 1 hr. to ensure that all the carbon was in solution or that there was no initial sensitization. All tests

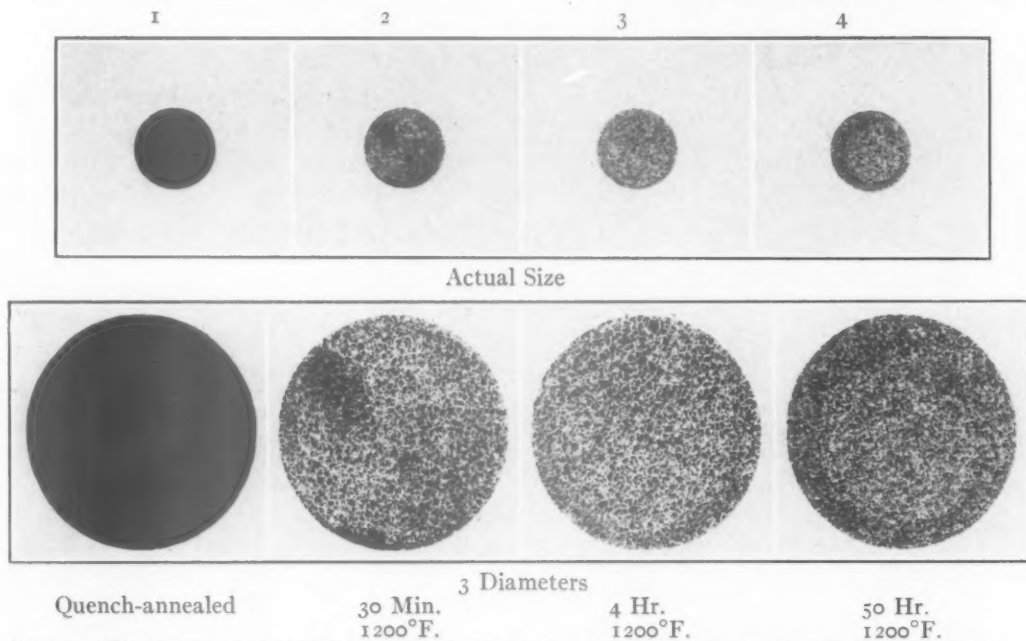


FIG. 2.—WROUGHT 18-8 SAMPLES HEAT-TREATED AS INDICATED AND SUBJECTED TO THE ELECTROLYTIC TEST. OBLIQUE LIGHT.

Analysis of steel is: Cr, 18.76 per cent; Ni, 8.46; C, 0.06; Si, 0.42; S, 0.022; Mn, 0.44; P, 0.018.

In most cases the presence of susceptibility to intergranular corrosion can be detected as a frostiness and grain-boundary attack, which is readily noticeable. Partial sensitization sometimes requires more careful examination, such as viewing at various angles or the use of a magnifying lens.

Most rolled or machined surfaces can be tested without any surface preparation except removal of grease or dirt. Cast surfaces, which usually are rough, are prepared by grinding a small flat spot and then polishing with a series of emery papers, to provide a fairly smooth surface. It is not necessary to remove all scratches.

RESULTS

Tests were made on wrought and cast stainless steels of various analyses after the samples had been subjected to the desired

were made with the sample initially at room temperature and using 13.9 amp. per sq. in. and $\frac{1}{8}$ in. between lead and steel panel.

WROUGHT STEELS TESTED

Progressive Sensitization.—Samples of wrought 18-8 steel of 0.06 per cent carbon content were sensitized by heating at 1200°F . for 5 min., 15 min. and 30 min., and 1 hr., 4 hr., 25 hr., 50 and 72 hr. Visual examination after the electrolytic treatment showed a definite increase in frosty appearance corresponding to the time of sensitization; that is, samples that had been held at 1200°F . for the longest periods of time showed the greatest frostiness. Fig. 2 includes photographs of some of these test spots at actual size and at 3 diameters, which reproduce fairly well the appearance of the spots when the sample is viewed

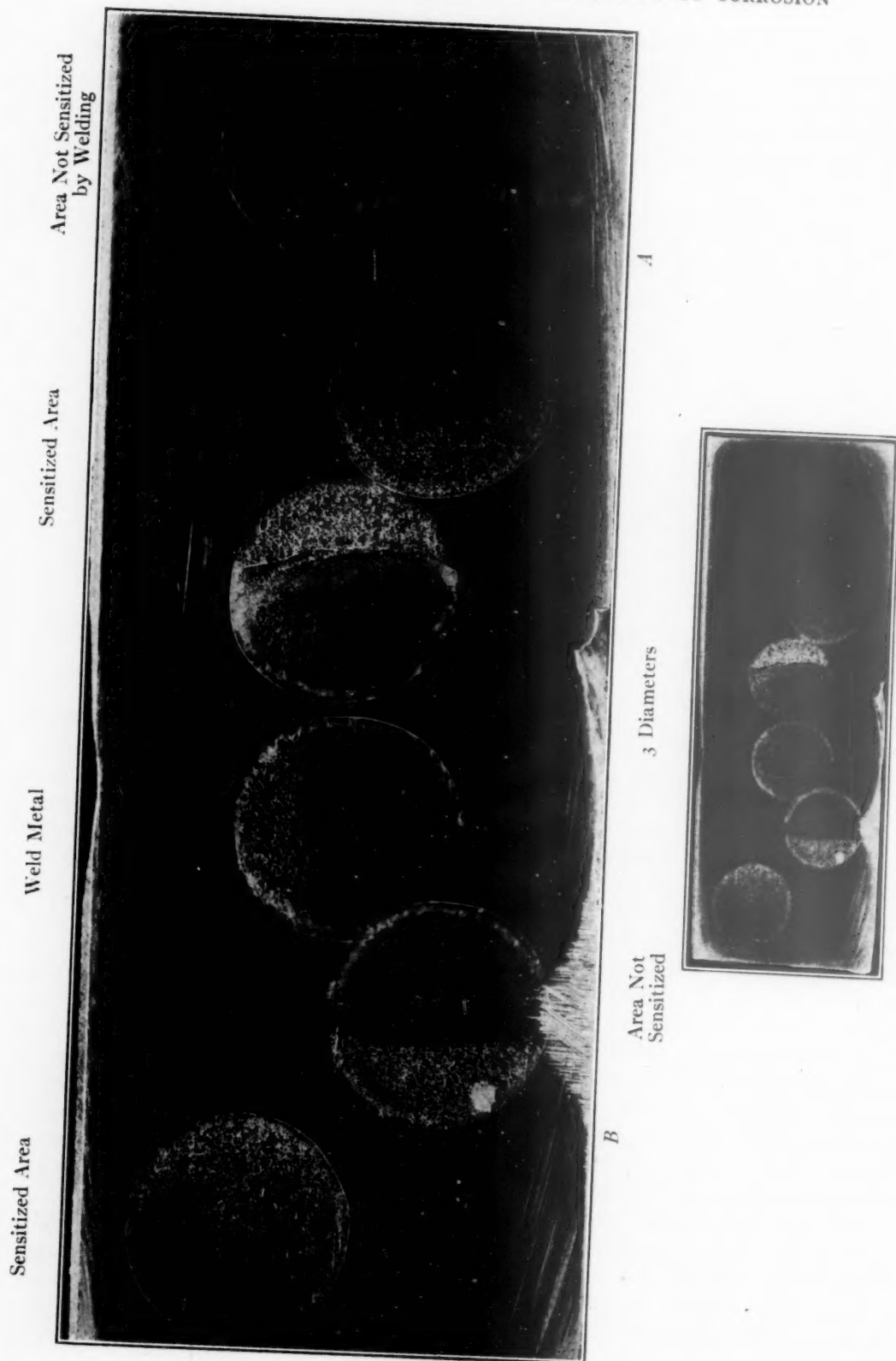


FIG. 3.—WELDED SECTIONS OF 18-8 STEEL OF 0.125 PER CENT CARBON.

obliquely. The heat-treatment given the sample illustrated is noted below the corresponding photograph and the chemical analysis of the steel used is included. The spot on the first sample, which was quench-annealed, appears almost black, which means that the spot was smoothly polished during the test. This smooth surface is a good reflector, and when viewed at an angle looks dark or black to the eye. Sensitized material does not give a smooth over-all finish but is rough at the grain boundaries. This is illustrated by the second sample, sensitized for 30 min. at 1200°F., which shows a definite outline of grain boundaries. This effect is produced by the scattering of the light at all angles at the rough areas, which have been selectively etched adjacent to the points of carbide precipitation; that is, the grain boundaries. The faces of the grains have been polished smoothly and appear as black areas. It is evident that the extent of carbide precipitation has increased with the time of heating at 1200°, because the spot on the sample heated for 50 hr. shows a very sandy finish and the absence of large reflecting grain surfaces. As mentioned above, it is possible to detect sensitization even after only 5 min. of heating. In fact, some tests to be described later show that sensitization produced by very short times of heating can be detected by the method.

Welds.—Fig. 3 includes photographs at actual size and at 3 diameters of 1-in. round steel sawed lengthwise, quench-annealed at 2100°F., welded together end to end, and then tested for sensitization at various points. The steel is 18-8 of 0.125 per cent carbon and the welding rod used was 18-8 of 0.07 per cent carbon. The photograph shows the sensitization produced adjacent to a weld. The photograph at 3 diameters is marked so that the areas of special interest can be noted. The line of demarcation between weld metal and adjacent steel is evident. On side *A* the sensitized zone in the steel is directly adjacent to the weld while

on side *B* there is a narrow portion beside the weld that is not sensitized. The probable explanation for this area is that the steel was heated above the sensitizing range at this point and cooled rapidly enough so that no carbide precipitation resulted. Note also the extent of the sensitized zone. It is about $\frac{3}{8}$ in. wide and beyond it the steel is in good condition, as is evidenced by the smooth polish observed on the third spot on side *A*. The white lines in this spot are due to grinding scratches only and cannot be mistaken for grain boundaries or sensitized areas. Also, a certain area in the weld shows sensitization. This was probably produced at the spot in the weld that was held in the sensitization range for the longest time.

A welded sample identical with that in Fig. 3 was quench-annealed at 2100°F. after being welded and was then tested for sensitization. The test showed no sensitization at any place and indicates that the susceptibility to intergranular corrosion can be removed by proper annealing.

Simulated Welds.—Steel panels $\frac{1}{8}$ and $\frac{3}{16}$ in. thick were heated by a torch at one end to a red heat (1100° to 1300°F.) for about 3 min. Such treatment is somewhat similar to that encountered in many welds. The panels were tested at various points and in all cases extensive sensitization was found in the heated portion.

Sensitizing Temperatures.—A complete investigation of the sensitization produced by heating at various temperatures was not attempted because the facts have already been amply reported. However, some samples heated at a few temperatures in the sensitizing region were studied.

Fig. 4 includes photographs at actual size and at 3 diameters of spots produced on samples of 18-8 steel of 0.05 per cent carbon. On sample 1, quench-annealed from 2100°F., the electrolytic treatment produced a smooth polish, which proves the absence of carbides or sensitization. The test spot shows extensive sensitization on sample 2, held at 1650°F. for 4 hr. Sample 3

was treated at 1200°F. for 4 hr. and shows that much more extensive sensitization is produced at this temperature. Sample 4 was heated at 1650°F. for 24 hr. This treatment dissolved the carbides. The photographs illustrate the smooth polish obtained and show that sensitization has disappeared. Sample 5 is piece No. 4 that was heated at 1200°F. for 4 hr. Sensitization has returned, although not to so great an extent as for No. 3. Apparently heat-treatment has greatly altered the grain size in the two samples.

The white dots and lines in sample 1 and 4 are caused by scratches in the surfaces produced in the original preparation with emery paper.

Effect of Columbium Addition.—It is known that the addition of certain carbide-forming elements such as columbium and titanium will remove the susceptibility to intergranular corrosion. Fig. 5 includes photographs of a wrought steel containing columbium. Sample 1 has been quench-annealed and sample 2 has been heated to 1200°F. for 2 hr. The electrolytic polish produced is the same in both cases. There is no evidence of carbide precipitation at the grain boundaries, this corresponding with the fact that the columbium does remove the susceptibility to intergranular corrosion. The white lines in the photographs are due to scratches from the polishing paper. The effect of titanium additions will be discussed later under cast materials.

Effect of Cold-work.—Rollason's^{13,14} studies of the effect of cold-rolling on intergranular corrosion of 18-8 show that cold-worked samples reach a maximum susceptibility to corrosion after a very short time of heating at the sensitizing temperature and will recover a resistance to corrosion after a few hours of heating at the same temperature. It is also known that annealed samples will reach their maximum susceptibility only after a long period of heating (300 hr.) and will recover after a much longer period (thousands of hours).

The present investigation included a brief study of these phenomena. A sample of 18-8 of 0.05 per cent carbon was cold-reduced 40 per cent. Pieces were then treated for various lengths of time at 1300°F. and were tested by the electrolytic method. The standard piece, cold-worked and untreated, gave a bright polish. The piece that was heated at 1300°F. for 2 min. gave a slightly dull polish, indicating the beginning of carbide precipitation. The piece heated for 5 min. gave a very frosty surface, and a microscopic examination showed carbides at the grain boundaries and the slip planes. Samples heated for 15 min., 1, 17, 30, 41, 48, 65, 72, 89, 98 and 115 hr. showed about the same degree of frostiness.

These results indicate either that the material was not restored to a state of resistance to corrosion or that the test cannot detect such resistance in this particular case. The latter seems more reasonable because the explanation of the renewal of resistance to corrosion of sensitized material is that the additional heating causes agglomeration of carbides with an accompanying diffusion of chromium, which replenishes the chromium-depleted portions, thus restoring the resistance to corrosion. In cold-worked material this agglomeration can take place more rapidly. It is, therefore, true that carbides will always be present in this case and it then seems likely that the test locates these carbides, just as in the other tests discussed the presence of carbides at the grain boundaries is detected. This in turn means that the test spot will be smooth and bright only when the carbon is in solution.

Cast Material

Progressive Sensitization.—Fig. 6 illustrates the progressive sensitization produced in samples of cast 18-8 steel of 0.04 per cent carbon content as the samples were treated at 1200°F. for increasing times. Sample 1 was quench-annealed from

2100° before testing. The surface of the test spot is not nearly as smooth as that for the corresponding sample of wrought material

the sensitized appearance, which shows definite grains and lines, as is illustrated by the other three samples in Fig. 6. The

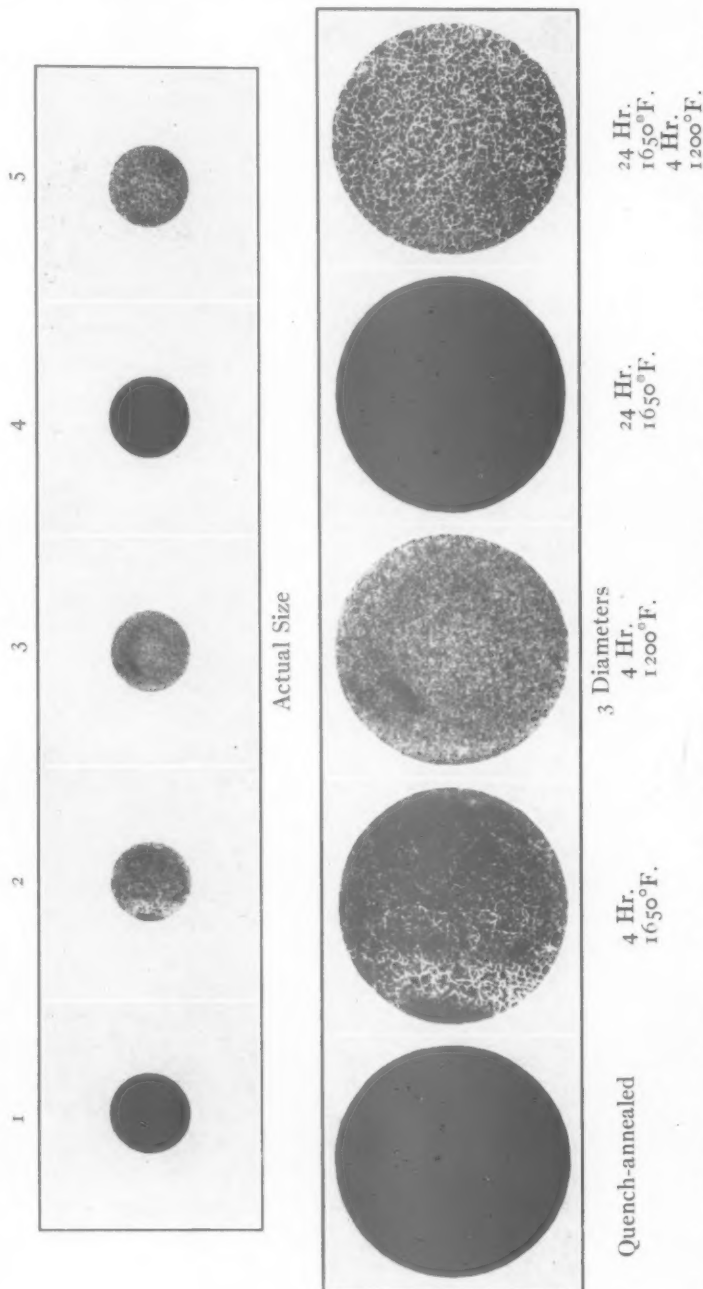


FIG. 4.—WROUGHT 18-8 STEEL OF 0.05 PER CENT CARBON HEAT-TREATED AS INDICATED AND TESTED FOR SENSITIZATION.

in Fig. 2. This unevenness in surface is characteristic of cast materials and is due to the dendritic formations present. The appearance can easily be differentiated from

progressive sensitization produced by heating at 1200°F. for 30 min., 4 hr., and 72 hr. is illustrated in samples 2, 3 and 4, respectively. The grain boundaries are definite

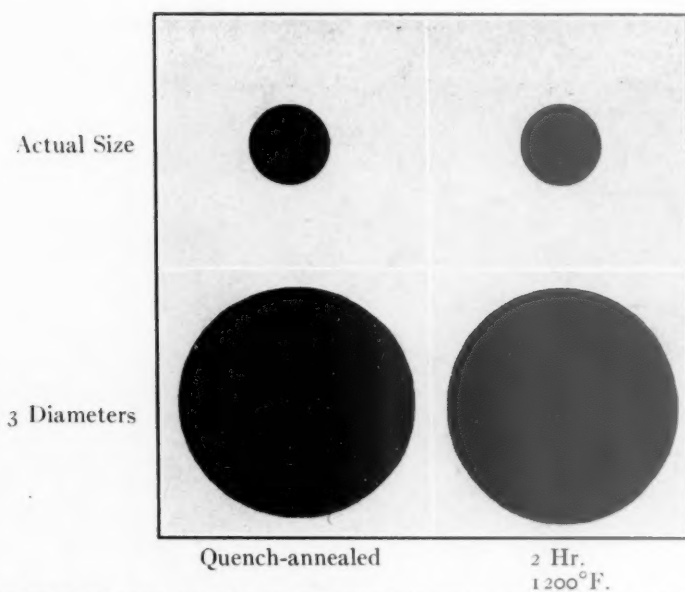


FIG. 5.—TEST SPOTS PRODUCED ON 18-8 STEEL SHOWING THAT ADDITION OF COLUMBIUM PREVENTS SENSITIZATION.

Analysis of steel is: Cr, 17.84 per cent; Ni, 9.74; C, 0.08; Cb, 0.85; Si, 0.51; Mn, 1.16.

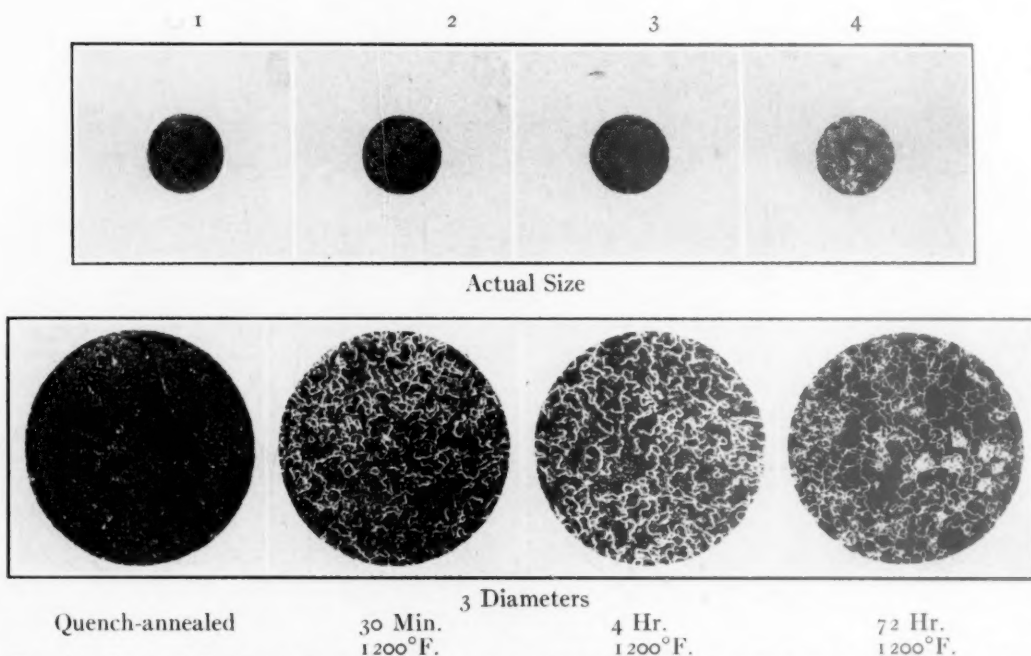


FIG. 6.—CAST 18-8 SAMPLES HEAT-TREATED AS INDICATED AND SUBJECTED TO THE ELECTROLYTIC TEST.

Analysis of steel is: 0.04 per cent C; 19.48, Cr; 8.96, Ni; 0.76, Mn; 1.09, Si; 0.10, Cu; 0.021, S; 0.016, P.

and the grains become more completely outlined as sensitization increases. There is also some indication of the formation of carbides within the grain, as shown by the white spots in No. 4.

0.10 per cent carbon were welded together and tested for sensitization at various points. Sensitized areas were found on each side of the weld in about the same location as those shown on side *B* in Fig. 3.

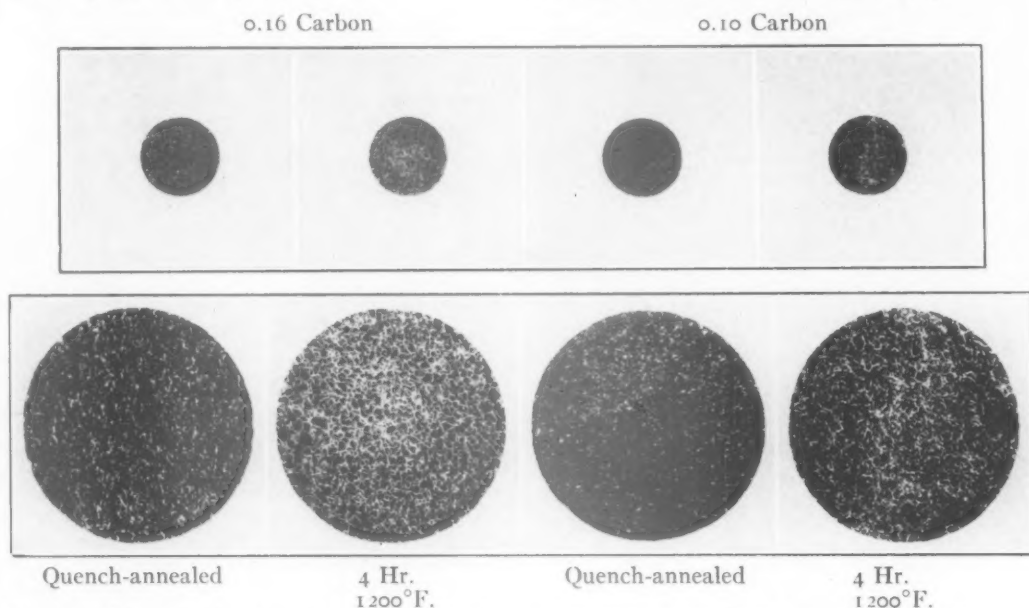


FIG. 7.—CAST 18-8 SAMPLES OF 0.10 AND 0.16 PER CENT CARBON HEAT-TREATED AS INDICATED AND TESTED FOR SENSITIZATION.

The larger grain size in the cast materials than in the wrought materials shown previously is evident. Indications also are that sensitization is produced more rapidly in large-grained material than in fine-grained.

Higher Carbon.—Cast samples of 18-8 containing 0.067, 0.10, 0.125, and 0.16 per cent carbon were treated for 4 hr. at 1200°F., and in all cases a differentiation could be shown between the sensitized and unsensitized material by means of the electrolytic test. Fig. 7 illustrates sensitized and unsensitized samples of 18-8 of 0.10 and 0.16 per cent carbon. The pictures illustrate that the distinguishing marking of sensitization is the outline of grain boundaries. Such a pattern is very different from that seen on the pieces that were quench-annealed. The patterns in these cases are due to the dendritic structure characteristic of cast materials.

Welds.—Two pieces of cast 18-8 steel of

Testing of Castings.—Fig. 8 illustrates a stainless-steel valve body that was tested by the method described above. The dark test spot free from grain-boundary lines indicates to the prospective user that the casting is free from carbide precipitation.

Effect of Molybdenum Addition.—Cast samples of 18-8 steel containing 3 per cent Mo with 0.04 and 0.10 per cent carbon were tested. The samples that were water-quenched from 2100°F. gave a fairly smooth polish, although not as bright as that for ordinary 18-8. Samples containing 0.04 per cent carbon and sensitized for 2 hr. at 1200°F. showed very little carbide precipitation, while samples containing 0.10 per cent carbon showed an extensive degree of precipitation after the same treatment.

Effect of Titanium Addition.—Cast samples of 18-8 steels containing 0.60 per cent Ti as a stabilizer were tested after quench-

annealing and after sensitizing at 1300°F . for 3 hr. In both cases a rough polish resulted. Fig. 9 illustrates the appearance of the spots. Neither one shows dark grains

ently titanium stabilizes by forming carbides and the test detects the presence of the carbides and shows them to be in the grain rather than at the boundary.

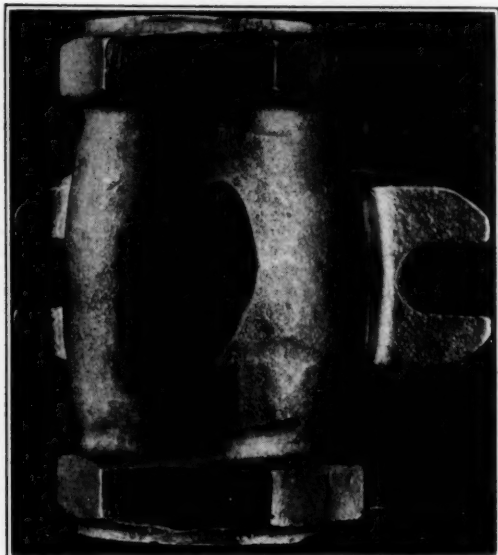
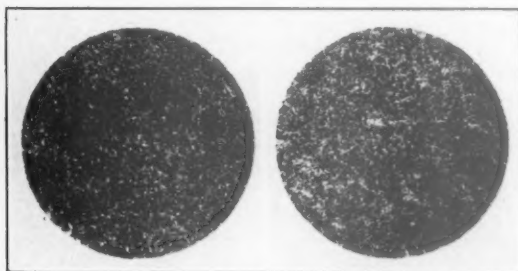
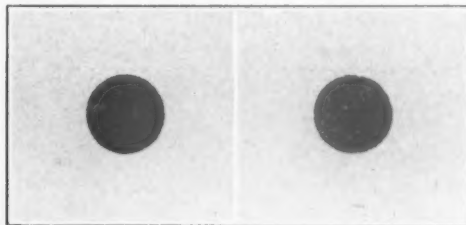


FIG. 8.—TEST SPOT ON 18-8 STAINLESS-STEEL CAST VALVE BODY.

Smooth polish as shown by black spot indicates freedom from sensitization.

outlined by white boundaries. A microscopic examination of these spots also shows the structure to be different from any found in the other steels. Also, in the titanium-steel samples the grains themselves seem to be etched and appear dark and rough. The grains in the sample that was sensitized at 1300°F . seem to be rougher than those in the quenched sample. The probable explanation for this result is that the titanium has formed carbides and the electrolytic test is picking out these carbides, which are present in both samples. However, the test does not indicate grain-boundary attack and therefore predicts that the steel is stable and not susceptible to intergranular attack.

Samples of the same steel were given a stabilizing treatment by heating for $2\frac{1}{2}$ hr. at 1560°F . One piece was then heated at 1200°F . for 2 hr. This piece and a stabilized one were tested and both showed spots similar to those illustrated in Fig. 9. Appar-



Quench-annealed 3 Hr. 1300°F .

FIG. 9.—TEST SPOTS ON SAMPLES OF 18-8 CONTAINING 0.60 PER CENT TITANIUM, ILLUSTRATING THAT TITANIUM STABILIZES AGAINST ATTACK AT GRAIN BOUNDARIES.

—Correlation with Corrosion Tests

At the time these tests were run no attempt was made to correlate the results with corrosion tests because it was felt that the conditions for producing sensitized materials had already been well established by previous workers. However, in connection with other work, some data have been obtained, which give a comparison of the results obtained by the spot test and by standard corrosion tests in acid solutions. Table 1 lists the percentage change in electrical resistance found in various wrought-steel samples after being subjected to a copper sulphate-sulphuric acid solution and to a 65 per cent nitric acid solution. These results are to be compared with those in column 5, which include the results of the electrolytic spot test. The spot test indicated susceptibility in all samples that later showed intergranular penetration in the corrosion studies. The low values in percentage change in electrical resistance of

1.2 and 1.5 in column 4 are not to be taken to indicate intergranular attack, because it was shown by weight-loss measurements that this was due to general attack.

ceptibility to intergranular corrosion. The formation of a smooth test spot indicates the lack of such susceptibility; and a spot that shows attack at areas other than the

TABLE 1.—Comparison of Susceptibility Tests on Wrought Materials

Sources	Alloy Type ^a	Percentage Change in Electrical Resistance ^b		Result of Electrolytic Test
		Boiling CuSO ₄ H ₂ SO ₄ 212 Hr.	Boiling 65 Per Cent HNO ₃ 212 Hr.	
Commercial.....	18-8 S	24	24 (48 hr.)	Susceptible
Commercial.....	18-8 S + Cb	0.0	1.2	Immune
Experimental.....	18-11 S	70	280	Susceptible
Experimental.....	18-11 S + Cb	0.0	1.2	Immune
Experimental.....	18-11 S + Ta	0.0	0.0	Immune
Experimental.....	18-11 S + Ta + Cb	0.0	1.5	Immune

^a All samples water-quenched from 2000°F., heated 3 hr. at 1650°F., air-cooled and heated 3 hr. at 1200°F.

^b Sample dimensions 4½ by ¼ by ⅛ inch.

The sulphate solution used was made up of 13 grams per liter of CuSO₄·5H₂O and 47 ml. per liter of H₂SO₄ (1.84 S.G.).

grain boundaries indicates carbide precipitation that may occur in a harmless form.

The cell is an open lead tube, one end of

TABLE 2.—Comparison of Susceptibility Tests on Cast Materials

Steel ^a	Treatment	Percentage Change in Electrical Resistance, Boiling CuSO ₄ H ₂ SO ₄			Result of Electrolytic Test
		24 hr.	90 hr.	163 hr.	
19-9.....	Quench-annealed	0.0	0.0	0.0	Immune
19-9.....	1200°F. 2½ hr.	320	1,400	22,100	Susceptible
19-9 + Cb.....	Quench-annealed	0.0	0.0	0.0	Immune
19-9 + Cb.....	1200°F. 2½ hr.	0.0	0.0	0.0	Immune
19-9 + Ti.....	Quench-annealed	0.0	0.0	0.0	Immune
19-9 + Ti.....	1200°F. 2½ hr.	0.0	0.0	0.0	Immune
19-9 + 3Mo.....	Quench-annealed	0.0	0.0	0.0	Immune
19-9 + 3Mo.....	1200°F. 2½ hr.	0.0	0.0	0.0	Immune

^a The steels contained 0.10 per cent carbon.

Table 2 is a similar comparison for cast materials. The spot test detected the one sample that later showed intergranular attack in the sulphate solution.

SUMMARY

A rapid electrolytic test has been developed for the detection of carbide precipitation in 18-8 steels. When the test is applied under proper conditions, and the spot produced is viewed by oblique illumination, the appearance of smooth dark grains outlined by bright boundaries indicates sus-

ceptibility to intergranular corrosion. The formation of a smooth test spot indicates the lack of such susceptibility; and a spot that shows attack at areas other than the grain boundaries indicates carbide precipitation that may occur in a harmless form.

The test appears to be applicable to both wrought and cast materials of various carbon contents. The effect of time and temperature on the degree of carbide

precipitation produced can be followed by the test.

It has been demonstrated that the test can be used to detect susceptibility to corrosion at points adjacent to welds.

The effect of addition elements on sensitization has been studied.

A brief study has been made of the effect of cold-work on carbide precipitation.

Photographs illustrating many of the above effects demonstrate that the naked eye is sufficient to differentiate between sensitized and unsensitized material that has been subjected to the test procedure.

The test is nondestructive and can be applied to completed structures.

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Some Experiments in the Production of Aluminum-nickel-iron Alloys by Powder Metallurgy

By P. R. KALISCHER*

(New York Meeting, February 1941)

IN the production of alloys by powder metallurgical processes it is often necessary or desirable to include one or more components that tend to form very stable oxides. Included in this group of metals are aluminum, manganese, magnesium, silicon, and a few others. In many cases it is not necessary for the sintered compact to have full density and the other physical characteristics of a cast alloy and in that event no undue precautions need be taken. If, however, it is required that the sintered part be entirely homogeneous, and have maximum density and physical properties, some method must be found to reduce the surface films of oxide, which are always present on the metals, and for the metals mentioned above this is always extremely difficult, if not impossible.

Since the production of high-density alloys is of particular interest to powder metallurgists, some experiments were undertaken to devise methods of reducing the refractory oxides. For this work, alloys of iron, nickel, and aluminum were chosen because aluminum oxide is one of the most stable oxides and because these alloys in the right compositions form excellent permanent magnets. All of the pertinent properties of the magnets could be accurately and delicately measured by density measurements and magnetic tests of sufficient scope

to give a complete demagnetization curve. From such a curve the maximum coercive force, residual magnetism, and energy products could be obtained and compared with the same properties for a cast material. Any lack of homogeneity, density, or solid diffusion would be immediately apparent as a decrease in the magnetic properties.

NATURE AND REMOVAL OF SURFACE BARRIERS

The early work of the present investigation was based upon published processes.* In the published information it was claimed that by intimately mixing iron, nickel, and iron-aluminum alloy (50 per cent Fe, 50 per cent Al) powders, compressing such a mixture into the desired shape and size, and then sintering (heating to a temperature below the melting point of the component metals) in hydrogen at 1200°C. or higher, a sound, homogeneous article could be made having the desired physical size, shape, and strength, and good magnetic characteristics. However, this early work showed clearly that something in the powder compress was inhibiting diffusion and the process was almost entirely unworkable.

In the initial phase of the investigation samples of iron powder, nickel powder, and iron-aluminum alloy powder were pressed into separate bars and sintered in hydrogen. Both the iron and nickel powders sintered

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* French Patent No. 799798; U. S. Patent No. 2192741.

to sound homogeneous masses, but the iron-aluminum alloy did not bond. It was assumed that the cause of the trouble was an aluminum oxide film, which formed

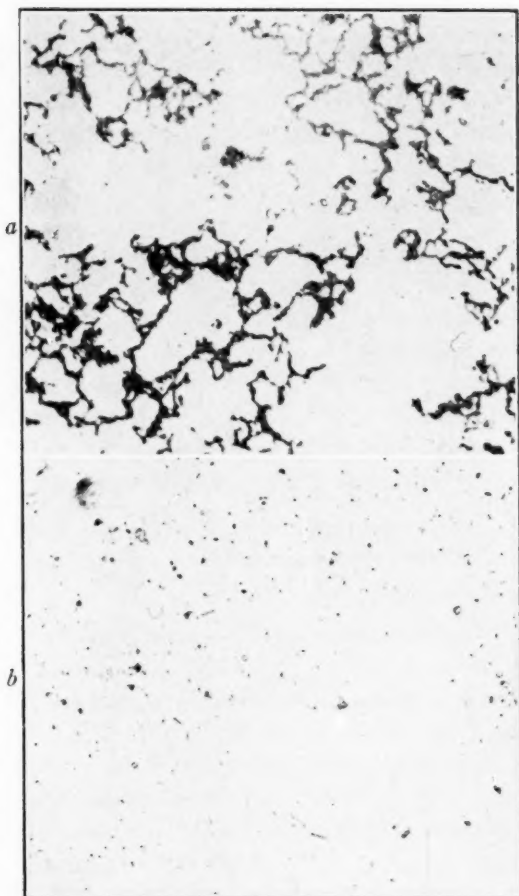


FIG. 1.—IRON-NICKEL-ALUMINUM ALLOYS MADE WITHOUT (a) AND WITH (b) TITANIUM HYDRIDE $\times 300$.

during grinding and could not be reduced.

Several methods might conceivably be used to prevent the formation of an oxide film, or to remove it:

1. Melt, cast and then grind to a powder the iron-nickel-aluminum alloy. Press the powder to the desired shape and size, and sinter under sufficiently reducing conditions.

2. Grind and store the iron-aluminum alloy under a protective gas blanket, such as nitrogen or hydrogen.

3. Grind and store the iron-aluminum alloy under an oil.

4. Impregnate a nickel-iron mixture pressed to size and shape with molten aluminum.

5. Dissolve the aluminum oxide film in some solvent and deposit a soft metal such as tin, nickel, or copper on the clean aluminum surface.

6. Reduce the aluminum oxide with atomic hydrogen.

Each of these six procedures was tried and the first five were found to be unworkable.

The use of atomic hydrogen as a reducing agent would unquestionably be satisfactory, but such a procedure requires that the hydrogen react with the aluminum oxide at the instant of generation, and this requirement immediately bars any of the more common methods of hydrogen generation. There are commercially available hydrides of titanium and zirconium (TiH_2 and ZrH_2); these are stable solids at room temperatures, but at about 450°C . they begin to evolve hydrogen, which, at the instant of evolution, is nascent—i.e., in the atomic state. This atomic hydrogen is an extremely powerful reducing agent, and it was thought that if an intimate mixture of one of the hydrides and the iron-aluminum alloy was heated, all or part of the oxide might be reduced.

Some titanium hydride was procured and a mixture of iron, nickel, iron-aluminum alloy and titanium hydride powders was made up, pressed into a bar and sintered at 1200°C . This bar showed some feeble magnetic properties, had a bright metallic fracture, and was fairly dense. The poor magnetic characteristics of the bar were not at all disappointing, since the composition was not optimum, and it was known that subsequent heat-treatment was necessary to produce maximum magnetic characteristics. The effect of the hydride is shown in the photomicrographs of Fig. 1. Fig. 1a shows an iron-nickel-aluminum mixture

without any hydride after sintering at 1200°C. From this it is apparent why the 2 per cent of titanium hydride was substituted for part of the iron. In this photo-

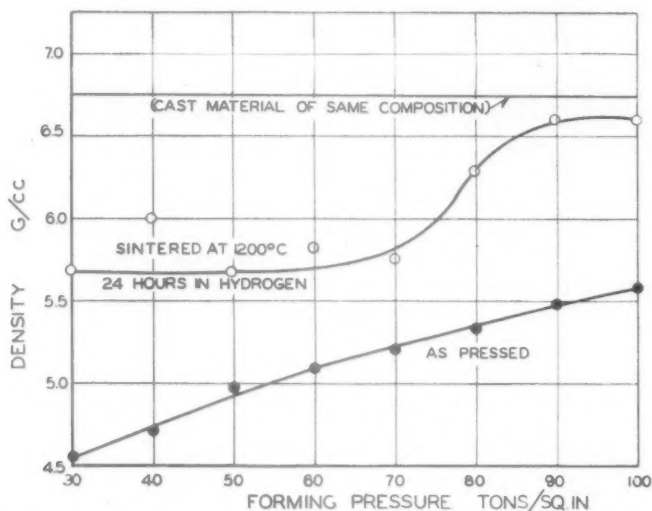


FIG. 2.—EFFECT OF FORMING PRESSURE ON DENSITY OF POWDER COMPACTS.

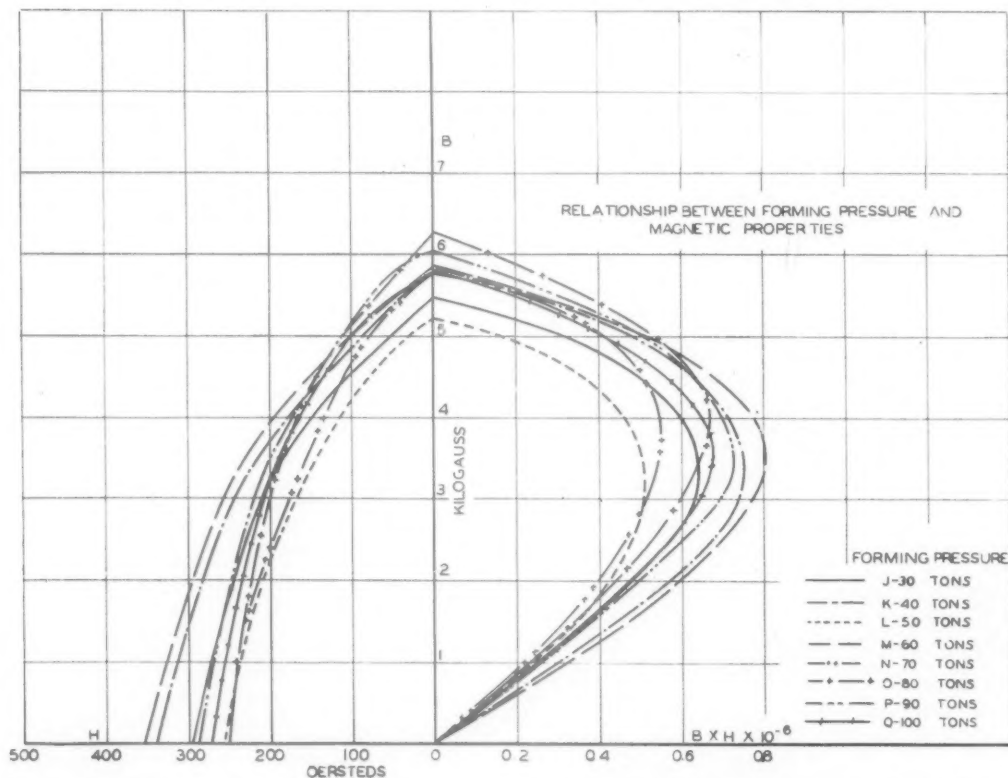


FIG. 3.—DEMAGNETIZATION AND ENERGY PRODUCTS FOR IRON-NICKEL-ALUMINUM MAGNETS. 25 per cent Ni, 10 per cent Al, 65 per cent Fe.

bars failed to sinter, since there is an almost continuous network of oxide. In Fig. 1b the same composition was used, except that

micrograph, only isolated particles of oxide are in evidence, and satisfactory sintering took place.

Having learned how to prepare a sound metallic bar reasonably free of oxides, the next phase of the investigation was to study the effect of forming pressure, sintering

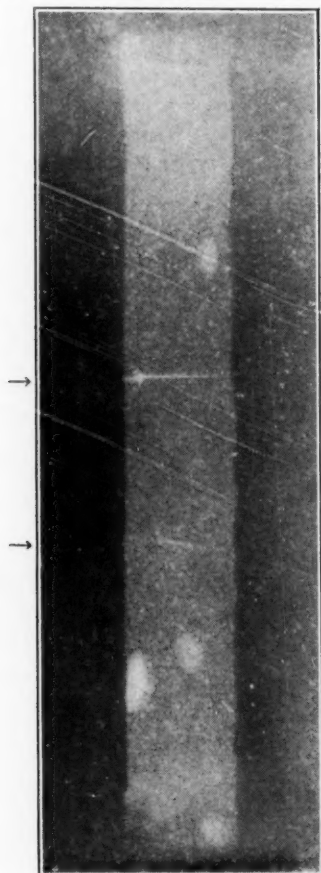


FIG. 4.—RADIOGRAPH OF MISHIMA MAGNET. Showing internal cracks caused by lack of die lubricant during pressing operation. None of the cracks appeared on the surface of the bar.

temperature, and time at temperature on the magnet material.

EFFECT OF PROCESSING VARIABLES

Forming Pressure.—In studying the effect of forming pressure, some fixed sintering time and temperature had to be chosen, and 24 hr. at 1200°C. was arbitrarily selected. Using standard composition* with the addition of 2 per cent titanium hydride, bars of standard size were pressed, using pressures from 30 tons per sq. in. to 100 tons per sq. in. The density and magnetic properties of

these bars are shown in Figs. 2 and 3. From Fig. 2, it is apparent that 90 tons per sq. in. is the minimum pressure that should be used in forming these bars. From Fig. 3, however, it would appear that 60 tons per sq. in. is optimum. This apparently anomalous condition was found to be due to the formation of small internal cracks during pressing (Fig. 4), and these cracks, which persisted through the sintering operation, while having little or no effect on the density, seriously impaired the magnetic properties. Later it was found that coating the die with Aquadag completely eliminated these cracks, so that the magnetic properties increased with increasing density. Based upon the results of these tests, a forming pressure of 100 tons per sq. in. was set as standard for all future work.

Sintering Temperature.—Utilizing a forming pressure of 100 tons per sq. in. and a sintering time of 24 hr. with standard composition, the effect of temperature was studied. Temperatures from 1100° to 1400°C. were used, and the samples were held at temperature for 24 hr. From the data in Table I it is apparent that the

TABLE I.—Effect of Temperature on Sintering of Iron-nickel-aluminum Alloys^a

TEMPERATURE, DEG. C.	DENSITY, GRAINS PER C.C. ^b
1100	Did not sinter
1200	6.60
1300	6.61
1400	Melted

* Nominal composition 25 per cent Ni, 10 per cent Al, 2 per cent TiH₂, balance Fe.

^b Density figures are average for three test pieces.

temperature range over which sintering can be done is narrow—from 1200° to 1300°C. Failure to secure sintering at 1100°C. can be explained on the basis of the low rate of solid diffusion of the particles at that temperature. If, however, a liquid phase were present, this diffusion would be stepped up. Since liquid phase of the iron-aluminum alloy can be secured at a temperature of about 1175°C., the reason for the success of the diffusion at 1200°C. is more apparent.

* See Appendix.

From this work a sintering temperature of 1200°C. was established.

Time at Sintering Temperature.—In

Summary.—In the foregoing sections, it has been shown that magnets of good density and with fair magnetic properties

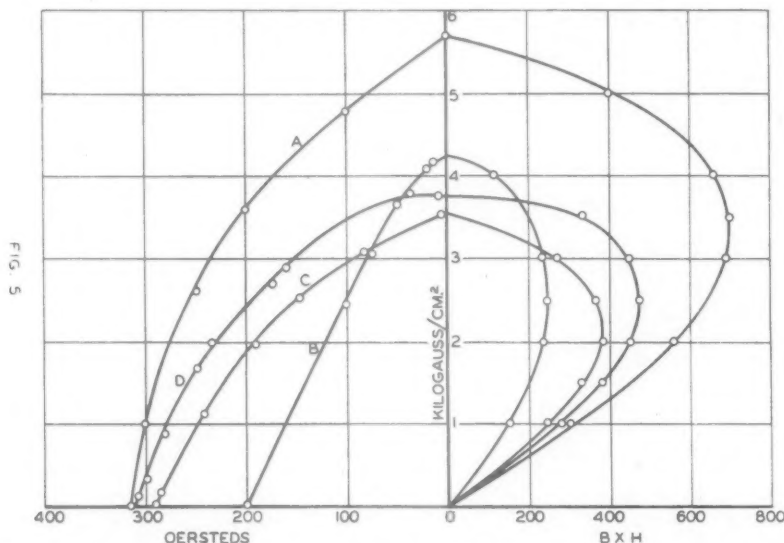


FIG. 5.—EFFECT OF TIME AT 1200°C. ON IRON-NICKEL-ALUMINUM MAGNETS. A, 20 hours; B, 5 hours; C, 10 hours; D, 15 hours.

studying the effect of time at sintering temperature, a forming pressure of 100 tons per sq. in. was used, with a sintering temperature of 1200°C. The composition was the same as in the two previous investigations. Time intervals from 5 to 40 hr. were used. The results are shown in Table 2 and

TABLE 2.—Effect of Time at Temperature on Sintering of Iron-nickel-aluminum Alloys^a

Number	Time-hours	Density, Grains per C.C. ^b
A	20	5.85
B	5	5.73
C	10	5.77
D	15	6.62
E	40	6.64

^a Forming pressure, 100 tons per sq. in.; sintering temperature, 1200°C. Nominal composition, 25 per cent Ni, 10 per cent Al, 2 per cent TiH₂, balance Fe.

^b Density figures average of three test pieces.

Fig. 5. The marked superiority of the sample sintered at 20 hr. is at once apparent. Longer sintering times up to 40 hr. were used, but the properties secured showed no superiority.

can be secured from powder compacts if the following conditions are met:

1. Presence of a metal hydride in the pressed bar to reduce the aluminum oxide.
2. A forming pressure of 90 to 100 tons per square inch.
3. A sintering temperature of 1200° to 1300°C.
4. A sintering time of 20 hr. or more.

EFFECT OF MOISTURE ON SINTERED PRODUCT

In all of the foregoing work, a carefully purified and dried hydrogen atmosphere was used in the furnace. The dew point of this atmosphere was held around minus 60°C. at all times, so as to prevent the formation of oxides from decomposition of water vapor at the sintering temperature.

With the use of the hydrides, however, it seemed possible that a gas atmosphere not quite so carefully purified and dried might be used. This phase of the work was investigated by varying the dew point of

the inlet gas to the sintering furnace from plus 20°C. to minus 70°C. The only bars successfully sintered were those in an atmosphere having a dew point of minus 50°C. or lower. At the higher water-vapor contents, a marked expansion of the test piece occurred, owing to the formation of a voluminous aluminum oxide phase. Where ever a high dew point was used, severe cracking of the bars accompanied the increase in size.

SHRINKAGE

Only the effects of the different factors involved in the sintering procedure on final density and magnetic properties have been considered.

During the sintering operation, a certain amount of shrinkage always occurs, and this shrinkage has great importance. Shrinkage can be defined as the percentage difference in volume between the pressed part and the sintered part. Throughout this work the amount of shrinkage of the test bars was checked, and by utilizing the

optimum conditions of pressure, time, and temperature, the amount of shrinkage during sintering was reduced to the minimum obtained, about 7 per cent of the volume as pressed. This figure cannot be taken as absolute, however, because the amount of shrinkage will vary with the size and shape of the part being sintered, and in general thicker pieces will shrink more than the thinner ones. No quantitative data are available on this particular point.

CONCLUSIONS

In the foregoing paragraphs it has been shown that powder metallurgical processes lend themselves well to the manufacture of complex alloys. The highly successful application of metal hydrides to the problem of reducing refractory metal oxides is particularly significant. The work has also shown the importance of both high unit pressures in forming and long enough time at the sintering temperature to allow solid diffusion to be complete, so that a completely homogeneous product results.

TABLE 3.—*Chemical and Physical Analyses of Powders Used*
IRON POWDER

Constituent	Per Cent	Size, Microns	Per Cent
Iron.....	98.40	40-50.....	2.17
Carbon.....	0.05	30-40.....	4.33
Silicon.....	0.03	20-30.....	16.20
Silicon dioxide.....	0.13	10-20.....	33.00
Other oxides.....	0.19 ^a	Less than 10.....	44.33

NICKEL POWDER

Nickel.....	98.70	40-50.....	1.26
Chromium.....	0.86	30-40.....	5.97
Silicon.....	0.02	20-30.....	19.98
Carbon.....	0.10	10-20.....	24.58
Iron.....	0.20	Less than 10.....	48.36

IRON-ALUMINUM ALLOY

Constituent	Cast Alloy, Per Cent	Thermit Alloy, Per Cent	Size, Microns	Per Cent
Aluminum.....	46.60	47.10	Larger than 50.....	0.3
Iron.....	48.80	51.20	25-50.....	2.0
Aluminum oxide.....	2.05	0.06	10-25.....	22.0
Silicon dioxide.....	1.02	0.01	2-10.....	76.0
Other oxides (by diff.).....	0.53	0.63		

^a Insoluble in dilute HCl.

APPENDIX

MATERIALS AND TEST METHODS

The hydrogen supply was from tanks of compressed gas. The gas was first passed over a nickel catalyst, held at 800°C. to convert any oxygen to water vapor. From the catalyst the gas passed through activated alumina, where the moisture content was reduced to a dew point of minus 50° to minus 60°C. From the drying tower the gas passed over calcium metal turnings held at 600°C., to strip any residual oxygen and water vapor from the gas, and thence into the sintering furnace. The entire purifying and drying system was maintained tight and operated at a small positive pressure to prevent infiltration of air or water vapor.

Throughout the entire work reported here, a standard-sized test bar was used; viz., 0.3 in. wide by 3 in. long, by about $\frac{3}{8}$ in. thick. Such a bar weighed 40 to 45 grams. The powders used were hydrogen-reduced iron powder, hydrogen-reduced nickel powder, and iron-aluminum alloy powder. All of the powders used passed through a 200-mesh screen. The iron-aluminum alloy was first made by melting and casting a 50 per cent Al alloy, followed by ball milling to pulverize it. Later, iron-aluminum alloy made by the Thermit process was employed, since the total oxide content was lower and the composition more nearly uniform than was secured by casting. (See Table 3 for analyses of the powder used.) A forming pressure of 30 tons per sq. in. was used in the early part of the work; later, a pressure of 100 tons per sq. in. was adopted as standard. All of the work was done on powder mixtures containing 10 per cent Al, 25 per cent Ni; balance, Fe.

Following tests for magnetic properties, the bars were broken and the fracture examined. A dull, black, nonmetallic fracture indicated that sintering had not been

successful, while a bright metallic fracture indicated successful sintering.

DISCUSSION

(R. M. Bozorth presiding)

F. C. KELLEY,* Schenectady, N. Y.—I cannot account for the apparently poor results

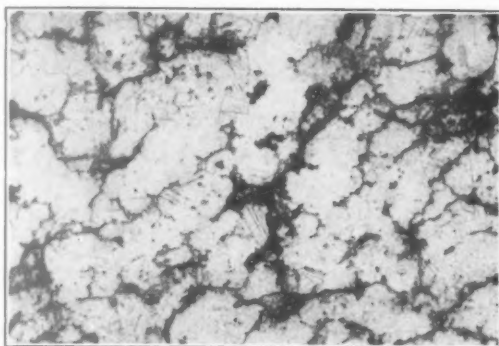


FIG. 6.—NICKEL-IRON BASE ALLOY PLUS 3.5 PER CENT TITANIUM HYDRIDE. $\times 100$.

obtained in the investigation reported by Mr. Kalischer. I am even more surprised at the better results obtained with the introduction of 2 per cent of titanium hydride.

The details in this process are very important, and there is no use in going into them at this time, for they have been fully revealed in the Howe patents mentioned in this paper as well as the published papers in *The Iron Age* [vol. 145 (1940) No. 2, pp. 27-31] and the Powder Metallurgy Conference at Massachusetts Institute of Technology, Aug. 29-31, 1940 (pages 180-183).

In Fig. 4 of Howe's paper in *The Iron Age* is shown a photomicrograph of our magnet material made by this process. Fig. 6 herewith shows a sintered nickel-iron base alloy to which 3.5 per cent of titanium hydride has been added. If a comparison is made with Figs. 1 and 2, respectively, in the paper under discussion, it will be noticed that our results appear to be directly opposite.

Titanium is an element with considerable activity toward oxygen and nitrogen and behaves much like aluminum in this respect.

It is rather difficult to see how atomic hydrogen released from the titanium hydride in a porous bar at 450°C. can do much to protect the aluminum in the powdered aluminum-iron

* Research Laboratory, General Electric Co.

master alloy at temperatures above this point. The master alloy is not subject to any severe degree of oxidation at this low temperature, and there is no shrinkage at this point to close the voids and thus seal the compact against diffusion of undesirable gases. In this case, it would seem that the active titanium metal would be just as much exposed to attack by oxygen or nitrogen as the aluminum in the master alloy.

The type of magnetic material in the Howe patents has been in commercial production for several years with very gratifying results. None of this material is formed at pressures above 30 tons per sq. in. It has been our experience that temperature can do more in bringing about maximum density than all the cold pressure that is practical to use. This temperature also favors high diffusion rates, thus bringing about equilibrium in a relatively short time.

The magnetic properties of the material given in Figs. 3 and 5 when compared with those given by Howe in Table 1 would seem to indicate that it is really possible to produce magnetic material of high quality by this process, and that some detail has been neglected by Mr. Kalischer, resulting in poor quality. The fact that he secures so much Al_2O_3 in his material tends to indicate that the trouble lies in the purity of the gas atmosphere.

F. V. LENEL,* Dayton, Ohio.—What kind of die was used in Mr. Kalischer's tests—one that can be taken apart after the powder is briquetted, or a solid die, which makes it necessary to push the briquetted test bar out through either the upper or lower opening of the die barrel?

There are some discrepancies between the results reported by Mr. Kalischer and those of the General Electric Co. According to Mr. Kalischer, a briquetting pressure of 90 tons per sq. in. is necessary to obtain theoretical or near-theoretical density in the sintered compacts; according to Mr. Kelley, 30 tons per sq. in. is sufficient for this purpose. I wonder whether the grade of powders used, particularly the grade of iron powder, may have something to do with this discrepancy. In our investigation of various grades of iron powder we found great differ-

ences in their behavior; some iron powders shrank very much more than others for a given briquetting pressure, sintering time and temperature.

Such an explanation would of course not help in answering the question whether an addition of titanium hydride is beneficial or detrimental in sintering iron-nickel-aluminum. This question seems to me to be of general interest; it may also have a bearing upon the problem of sintering other easily oxidizable metal powders. Therefore, I hope that further work will be done to solve the present apparent discrepancies.

W. E. KINGSTON,* Emporium, Pa.—While our experience has been only in the production of nickel-aluminum alloys by powder metallurgy, in general our results have agreed with Mr. Kalischer's. We have the same problem in so far as prevention of oxidation of the aluminum during preparation and sintering of the compacts. This is extremely important in our case since our alloys are eventually drawn down to wire, perhaps less than one thousandths of an inch in diameter, and the formation of any of the aluminum compounds such as Al_2O_3 or Ni_3Al , both of which are hard, brittle components, effectively prevents cold-drawing of the alloy in the smaller size of wire. Our experience has covered a wide range of aluminum in nickel, and it is necessary in alloys of this type to hold the aluminum content below the point at which a second phase is present, otherwise all of the aluminum must be in solid solution with the nickel.

We have found that it is extremely important to prevent the formation of water vapor in the furnace during sintering. This water vapor may be present for several reasons. In the first place, it may be present in the hydrogen atmosphere as water vapor, and I note that Mr. Kalischer has very carefully dehumidified his gas. Secondly, it may be present because of leakage of air into the sintering furnace, which combines with the hydrogen to form water vapor, which at certain temperatures allows the formation of Al_2O_3 in the compacts. Thirdly, it may very readily be formed by the degassing of the compact itself during sintering; since these pressed

* Moraine Products Division, General Motors Corporation.

* Chief Metallurgist, Hygrade Sylvania Corporation.

compacts always contain large amounts of absorbed gases, and during sintering these gases are usually thrown out, and since in many cases these gases contain oxygen or oxygen compounds they may very readily combine with hydrogen to form water vapor and thus cause the compound Al_2O_3 to form. In our particular work, we have found that it is necessary to take care of all three of these factors very carefully. In the first place, the aluminum and nickel powders are very carefully ball-milled in an inert atmosphere in order to prevent further oxidation of the aluminum powder. Nitrogen is usually employed as the atmosphere in this case. The compacts are then pressed and sintered in a large vacuum furnace. During the first stage of sintering the pressure in the furnace is maintained at less than 10 microns until a temperature of around 800°C . is reached. During this time gases coming from the compact itself are pumped out. The point where practically all of the gas is removed from the compact is indicated by the dropping of the pressure to perhaps one micron. Then hydrogen or argon is admitted into the furnace and the remainder of the sintering takes place under this atmosphere. This hydrogen or argon is purified in substantially the same manner that Mr. Kalischer employed in his work. These compacts after this treatment show no indication of any Al_2O_3 and when the aluminum component is held within certain limits, there is no indication of the compound Ni_3Al forming. Such alloys are extremely ductile and can easily be cold-worked into very small sizes. Microstructures of these alloys show almost no voids, or presence of compounds.

We agree with Mr. Kalischer that the use of titanium and zirconium hydrides may help to prevent the formation of these undesirable oxides of aluminum. We have found this to be true with the nickel-aluminum alloys prepared by powder metallurgy. There we found that the technique of sintering was perhaps not as critical when the zirconium and titanium hydrides were used. In our particular work, however, these hydrides were undesirable for other reasons and we found the method described

above for the prevention of the formation of the oxides of aluminum to be very satisfactory.

We also found that if the sintering temperature is advanced to within 95 per cent of the melting point of the alloy, densities of 90 per cent of cast metal may be obtained, and after hot-working and cold-working the density of the sintered alloy equals that of the cast alloy.

P. R. KALISCHER (author's reply).—I assume that Mr. Kelley, in referring to the "apparently poor results obtained," is speaking of the magnetic properties as reported. If so, apparently he has missed the point of the paper. Magnetic tests were used as an indication of homogeneity, completeness of sintering, soundness, and other physical properties of the alloy, and at no time was an attempt made to determine optimum composition and heat-treatment after sintering to secure the best magnetic properties.

Titanium hydride *starts* to evolve hydrogen at 450°C . and this evolution continues at the higher temperatures. According to information furnished by the producers of this material, the hydrogen evolution continues even at temperatures above those used in sintering iron-nickel-aluminum alloys.

While it is unquestionably true that dense material can be secured if low forming pressures and high sintering temperatures are used, it is also true that there will be a high volumetric shrinkage and considerable warpage associated with this procedure—both of which are most undesirable. It is also true that the use of lower forming pressures requires higher sintering temperatures, another undesirable feature from furnace design, maintenance, and operational standpoints. The higher diffusion rate at the higher temperatures is, of course, an advantage.

Replying to Mr. Lenel, the die used could be taken apart so that the test bars did not have to be ejected through the die barrel.

The type of powder used in pressing operations is most important. In our work we used annealed iron powder having quite a low oxide content.

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